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METHANOL AS AN AUTOMOTIVE FUEL:
A SUMMARY OF RESEARCH IN THE M.I.T.
ENERGY LABORATORY

Energy Laboratory Report
No. MIT-EL 76-013
April 1976

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1. INTRODUCTION

Methanol as an alternative to many fuels derived from petroleum is receiving considerable and increasing national attention. It has been suggested that the conversion of natural gas available at remote locations to methanol, may resolve many of the difficulties associated with natural gas transportation. Methanol can be made from municipal and other organic waste materials which currently go unused. Methanol from coal is a potential major future source of liquid fuel to replace today's petroleum products.

If methanol becomes competitive with other forms of liquid fuel energy, it could be used in a number of applications. One of these is a motor vehicle fuel, and both the use of methanol-gasoline blends and methanol alone have been proposed. In this potential application it is important to ask whether methanol has special characteristics which offer advantages, or create major problem areas, relative to conventional or synthetic gasoline. The work described in this report focuses primarily on these questions.

In early 1974, in large part because of the efforts of Dr. T.B. Reed of M.I.T.'s Lincoln Laboratory to demonstrate that methanol-gasoline blends could be used in the automobiles in actual use today, Mr. J.B. Hawley Jr. made a \$100,000 grant to the M.I.T. Energy Laboratory to stimulate a number of methanol related activities. Plans for a range of research topics were developed, and by June, 1974, the following areas had been selected as parts of the Energy Laboratory methanol program to be funded from this source. These were: (i) the operation of a methanol information center

to provide advice and dispense information in response to the substantial number of requests which were being received; (ii) basic internal combustion engine studies to identify the differences between gasoline, methanol-gasoline blends, and methanol as automotive fuels; (iii) a study of the phase stability of methanol-gasoline-water blends, an area of great importance in methanol fuel handling and storage; and (iv) the development of a detailed proposal for an automobile fleet test program designed to identify the advantages and disadvantages of methanol-gasoline blends as compared to gasoline fuel alone. These activities were all initiated in 1974 and have now been completed. The \$100,000 Hawley grant was supplemented with additional Energy Laboratory grant funds. The expectation was that these initial research activities would lead to proposals for funding for more extensive work on methanol as an automobile fuel at M.I.T.

The following sections of this report describe the status of work on methanol completed to date within the Energy Laboratory. Section 2 briefly reviews the current status of our knowledge of methanol as an automotive fuel. Section 3 describes the results of the single cylinder engine experiments with gasoline, methanol-gasoline blends and methanol. Section 4 reports on the work on physical properties of methanol-gasoline blends. Section 5 summarizes the information and proposal activities of the methanol group. Section 6 describes the development of the proposal for the fleet test program. Section 7 summarizes the major findings of this work.

A proposal to extend the basic research activities on properties of methanol-gasoline blends, and the operating and emissions characteristics of these fuels in spark-ignition engines was developed and submitted to the National Science Foundation and Energy Research and Development Administration during 1975. Unfortunately, due to limited government support available for work in these areas, the proposal has not yet been funded.

A detailed proposal for the fleet test program was developed, and arrangements for procuring fuels, for a fuel storage and distribution site, for laboratory space for working on test vehicles and the development of suitable instrumentation had been initiated. Over the six-month period from June 1974 to December 1975, substantial efforts to obtain external funding for the actual carrying out of the fleet test program proved unsuccessful. In December 1975, the Energy Laboratory reviewed the prospects of obtaining the necessary funding, examined the technical value of the proposed fleet test with the current mix of in-use automobiles given the likely time-frame on which methanol might become available for automobile use, and assessed the general suitability of such a demonstration program in the M.I.T. academic community. For reasons related to all these considerations, it was decided not to pursue the fleet test activity as a major Energy Laboratory program.

A number of positive conclusions, and more precise identification of several problem areas in need for further research, have come out of the methanol program to date. These are summarized in Section 7.

2. METHANOL AS AN AUTOMOTIVE FUEL: A REVIEW

The possibility of using alcohols for motor fuels, either in their pure form or blended with gasoline, has been considered from time to time over the past forty years. Current energy shortages have renewed the interest in alcohols as fuels for spark-ignition engines. Specifically, methanol has become the topic of much research since it can be derived from coal at costs comparable to the cost of synthetic gasolines. Experimental results have been published which suggest significant gains in fuel economy when the properties of methanol are fully realized. The disadvantages in using pure methanol or methanol-gasoline blends stem from the observed problems of material compatibility, increased volatility and phase separation. The following sections briefly describe some of the known advantages and disadvantages of methanol as a motor vehicle fuel.

Cost and Availability of Methanol

The cost of producing methanol has been estimated by a variety of sources to lie in the range of 1.0 to 1.5 times the current cost of gasoline on an energy unit basis ^(1,2). This large range is attributable to differences in assumed geographic and raw material sources. A recent study ⁽³⁾ projects that the cost of methanol versus synthetic gasolines derived from domestic coal and shale resources are in the ratio of about 1.1 through the year 2000. This cost penalty may be more than offset if the postulated energy gains due to methanol usage materialize.

Availability is probably the limiting factor to large-scale use of methanol as a motor fuel. The Atomic Energy Commission ⁽²⁾ projects that

with "sufficient effort" it would be possible to produce only 3% of the gasoline energy market by 1980. At this level the impact of methanol would be minimal. It appears that methanol, even under the most favorable conditions, could only contribute significantly to the national energy or environmental situations in the post-1985 time-frame.

Material Compatability, Distribution and Properties

Several engineering problems associated with the use of methanol and methanol gasoline blends have arisen as a result of extensive vehicle tests ^(4,5). Material compatability is usually associated with fuel system components. Of these components copper and brass are the most susceptible to corrosion problems when methanol is used. Rubbers such as Buna-N or Neoprene were not affected by methanol use.

The properties of methanol, specifically its high volatility and affinity for water, pose problems of driveability and phase separation, respectively. If methanol or methanol-gasoline blends are used in current production vehicles, significant cold start driveability problems can occur ^(4,5,6). It is the opinion of most investigators that such problems are not insurmountable.

Phase separation in the fuel is more serious since distribution systems would have to be kept water tight. Phase separation can occur when as little as 0.1 to 0.2% of water is present. High alcohols may have to be used to stabilize gasoline-methanol blends in the presence of water.

Experiments with Methanol as a Motor Fuel

Single cylinder and multi-cylinder engine experiments using pure methanol as a fuel show that methanol burns more energy efficient, at leaner air-fuel ratios, and at higher compression ratios without detonation than commercial gasoline (7,8,9). The use of methanol-water blends has been proposed as a means for increasing engine compression ratios while maintaining low nitric oxide emissions (8,9). Using the beneficial properties of methanol, estimates of a 20% increase in energy economy are postulated (8). Although data on the optimum use of methanol in spark-ignition engines is preliminary, the results are encouraging. Methanol blends with gasoline show little or no gains in fuel efficiency when allowance for equivalence ratio change is made (4,5). This should not be viewed as a disadvantage, since methanol could be introduced into the market gradually with no penalty to energy efficiency. However, distribution and driveability problems would have to be solved first.

Several fleet tests using methanol-gasoline blends have been completed (4,5,6). These tests document the problems associated with using methanol blends. The most severe problem is driveability, especially during cold operation and accelerations. Although this is an important problem, there is general agreement that the problems associated with methanol usage are not insurmountable.

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3. BASIC ENGINE STUDIES ON METHANOL AND METHANOL-GASOLINE BLENDS

It has long been known that alcohols and alcohol blends have properties as spark-ignition fuels which are different from gasoline alone. Both methanol and methanol blends with gasoline have shown that fuel economy and emission characteristics can be altered significantly from that of pure gasoline. The physical explanations for these differences have not always been obvious due to parameter changes that occurred during the course of changing fuels. For example, if no adjustments are made to the carburetor, changes in the air-fuel ratio usually occur. The goals of the "basic engine studies" were to determine if methanol, methanol-gasoline, or methanol water blends had a distinct advantage over gasoline with regards to emissions and energy efficiency and to determine the reasons for the observed differences in performance. In addition, information for a detailed data base on these fuels would be accumulated as a result of the experiments.

Experimental Apparatus and Procedures

A standard cooperative fuels research (CFR) engine was used as the test engine. The engine was equipped with a shrouded valve so that combustion characteristics similar to conventional engines could be obtained. Air flow into the engine was measured using a standard ASME square edged orifice and the fuel flow was measured using a rotometer. Fuel and air were pre-mixed in a large heated mixing tank to insure that a homogeneous, constant temperature charge was supplied to the engine. The engine was instrumented with a piezoelectric pressure transducer and crank angle indicator in addition to the standard instrumentation for measuring torque, inlet pressures, and temperatures. An engine load of 50 psi indicated mean effective pressure (imep) at 1600 RMP was chosen as the operating point

since it is representative of a modest vehicle acceleration on the Federal test procedure.

The main tasks for these experiments was a determination of the combustion characteristics for the different fuels. The combustion was characterized by the ignition delay time, combustion duration, fuel economy (energy efficiency), and emissions at the minimum spark advance for best torque (MBT) and a given equivalence ratio. Another important parameter, the lean misfire limit, was also studied. A piezoelectric pressure transducer was installed in the engine to obtain accurate cylinder pressure versus time data at each operating point. This data was analyzed to obtain the mass fraction burned versus crank angle curve from which the ignition delay and combustion duration are obtained.

Results

A comparison of the emission characteristics of the four fuels studied is shown in Figures 1-3. The hydrocarbon (HC) emissions expressed in terms of unburned fuel are shown in Figure 1. This figure indicates that the unburned fuel emissions from methanol and blends of methanol with water and indolene are higher than that of pure indolene for lean engine operation. For rich stoichiometries, no differences were observed. In Figure 2, the carbon monoxide (CO) emissions are presented. No appreciable differences in CO emissions were observed although the CO emissions for methanol appeared lower at lean equivalence ratios. The most dramatic differences in emissions occurred for nitric oxides (NO) and are shown in Figure 3. The NO emissions for methanol and the methanol/10% water blend are considerably lower than those for indolene. This is to be expected since methanol and methanol/10% water have lower adiabatic flame temperatures than indolene.

The differences in the indolene and indolene/methanol blend are negligible on the lean side of stoichiometric, and the indolene/methanol blend has slightly larger NO emissions higher for rich operation. This may be due to the excess oxygen carried by the methanol. Note that at an equivalence ratio of 0.7 the NO emissions for methanol are 3 times lower and the methanol/water blend are 10 times lower than those for indolene. In addition, engine operation with methanol in this region is more reliable than with indolene as is indicated by the lean limits of the fuels.

A comparison of the indicated specific energy efficiencies of indolene, indolene/15% methanol, methanol, and methanol/10% water is shown in Figure 4. The thermal efficiencies for indolene and the indolene/15% methanol blend are essentially equivalent at all air-fuel ratios. This indicates that there is no inherent efficiency advantage to the gasoline-methanol blends. Pure methanol showed the highest thermal efficiency and the methanol/water blend the lowest. However, a higher thermal efficiency can be obtained for the methanol/water blend by using higher compression ratios. This will be discussed later in this section. The lean limits of the four fuels are also shown in Figure 4. Methanol has the lowest lean limit followed by the methanol water blend. This characteristic can be exploited both for efficiency and emissions improvements. The thermal efficiency for methanol is from 4-5% greater than that of indolene. This improvement in efficiency can be due to shorter combustion durations or an increase in the ratio of specific heats. The latter was investigated using the NASA Equilibrium program for determining the ratio of specific heats for the burned products of the two fuels. At a pressure of 30 atm. and temperature of 2200 °K the ratio of specific heats for methanol and indolene were 1.21

and 1.22 respectively. This difference cannot explain the observed improvement in efficiency.

Another possible difference between the methanol fuels and the indolene could occur in the turbulent flame speeds. One measure of this is the combustion duration of each fuel at a given equivalence ratio. To obtain the combustion durations the cylinder pressure-time diagram is analyzed to obtain a mass fraction burned versus crank angle curve (see Figure 5). The combustion duration is defined as the crank angle interval for 10 - 90% of the charge to burn. The ignition delay is defined as the crank angle interval for 0 - 10% of the mass to burn. Figures 6 and 7 show the combustion durations and ignition delays for the four fuels. The shorter combustion duration and ignition delays for methanol are possible reasons for the observed improvement in thermal efficiency. Besides the shorter combustion duration of methanol, reduced heat transfer to the cylinder walls due to lower combustion temperature may be a major contributor to the increased efficiency of methanol.

The low NO emissions for the methanol and methanol/water blend led to an investigation of improvements in efficiency when the compression ratio is increased. Figures 8 - 11 show the results of this study. For these tests the compression ratio was increased for MBT spark up to the point of incipient knock. For all the runs the energy efficiency and HC emissions increased as the compression ratio was raised. NO emissions showed mixed trends but, in general, did not increase significantly. Figure 11 indicates that the methanol/water blend could be run at a compression ratio of 10 and have an equivalent energy efficiency to indolene at the base condition

as well as NO emissions that were 7 times lower. Unfortunately, HC emissions were also increased. Data such as that presented in Figures 8-11 can be used to develop trade-offs between fuel economy and emissions and are a necessary part of a data base on methanol fuels.

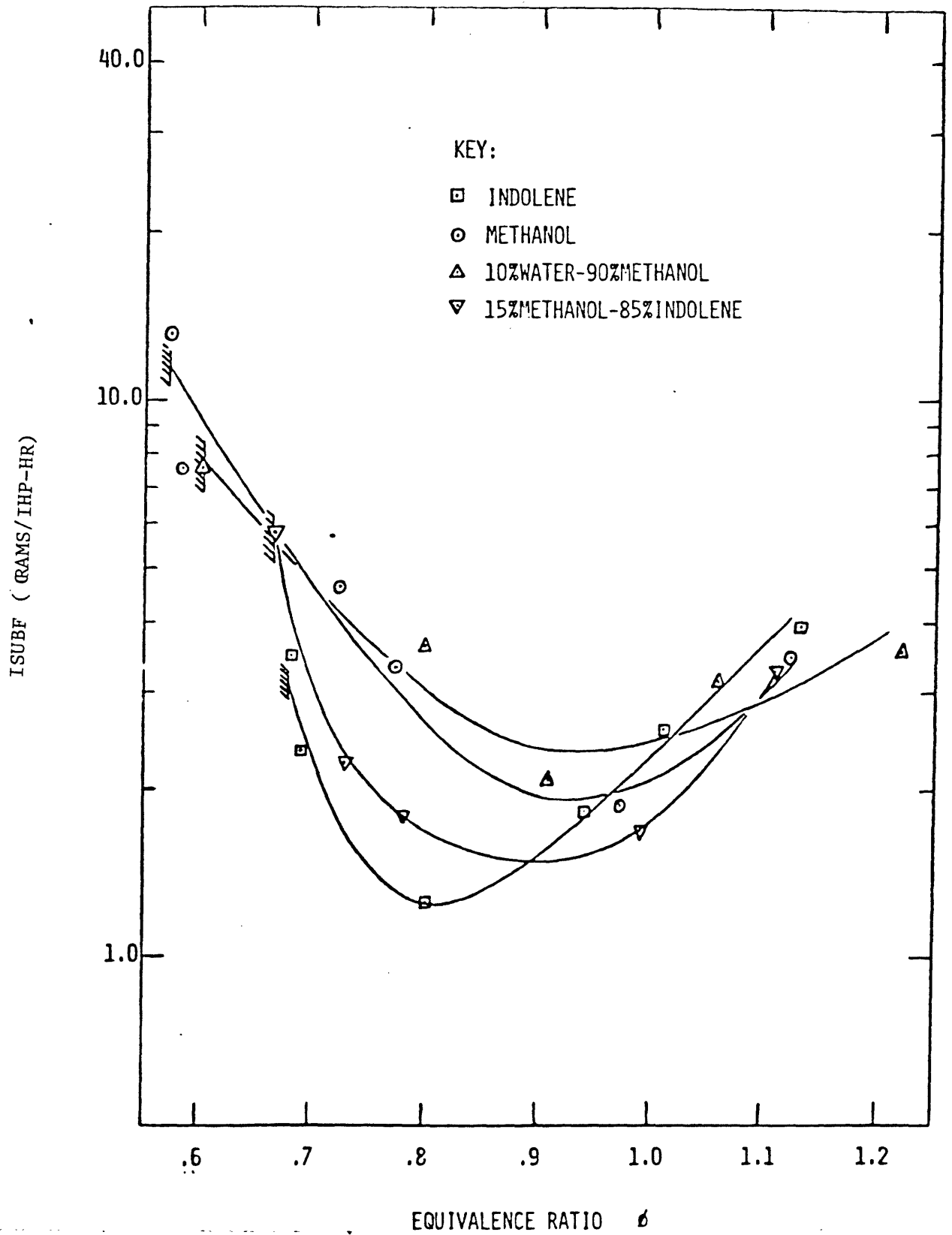


Figure 1 Indicated specific unburned fuel emissions (ISUBF) vs equivalence ratio (ϕ) and fuel type

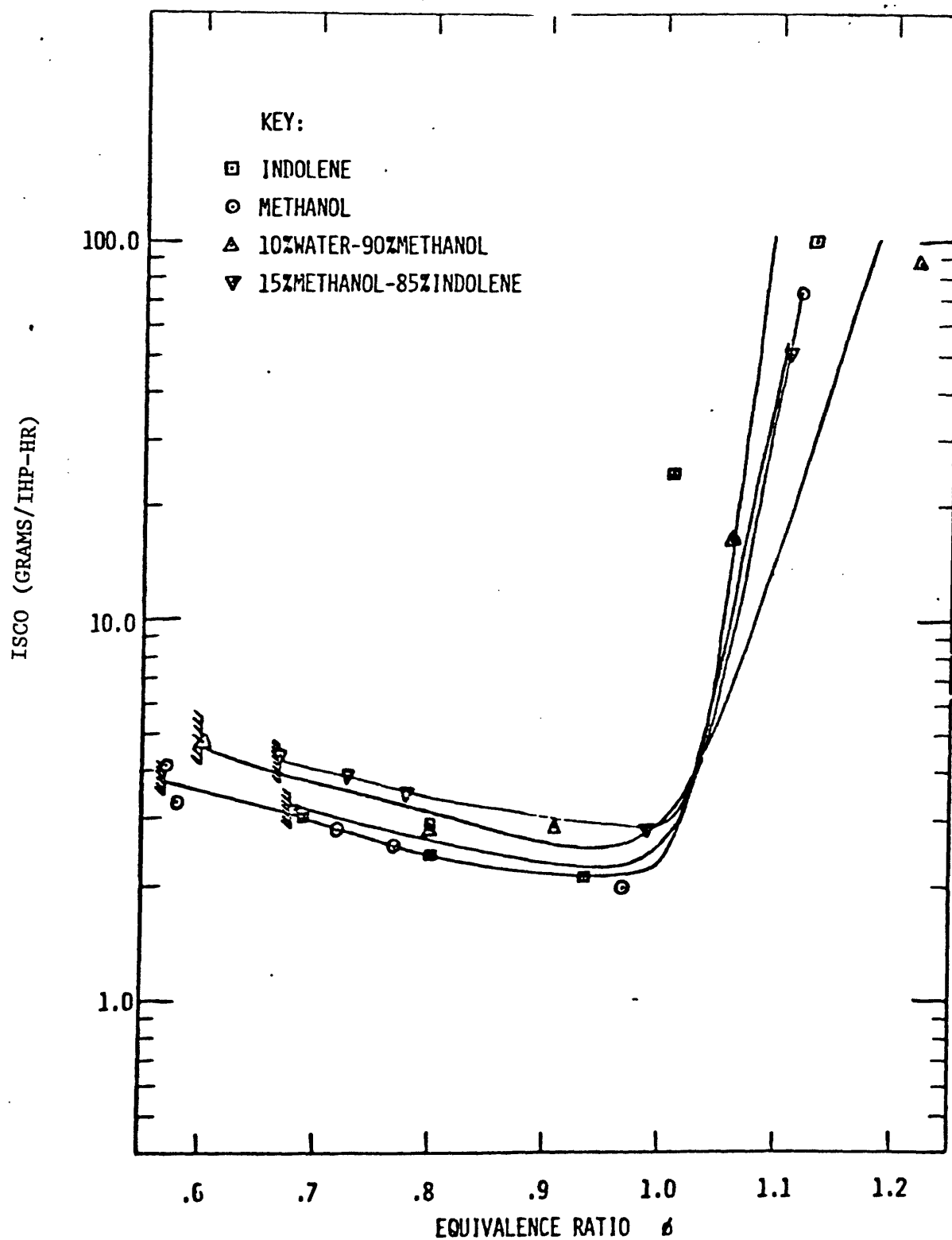


Figure 2 Indicated specific carbon monoxide emissions (ISCO) vs equivalence ratio (ϕ) and fuel type at baseline conditions

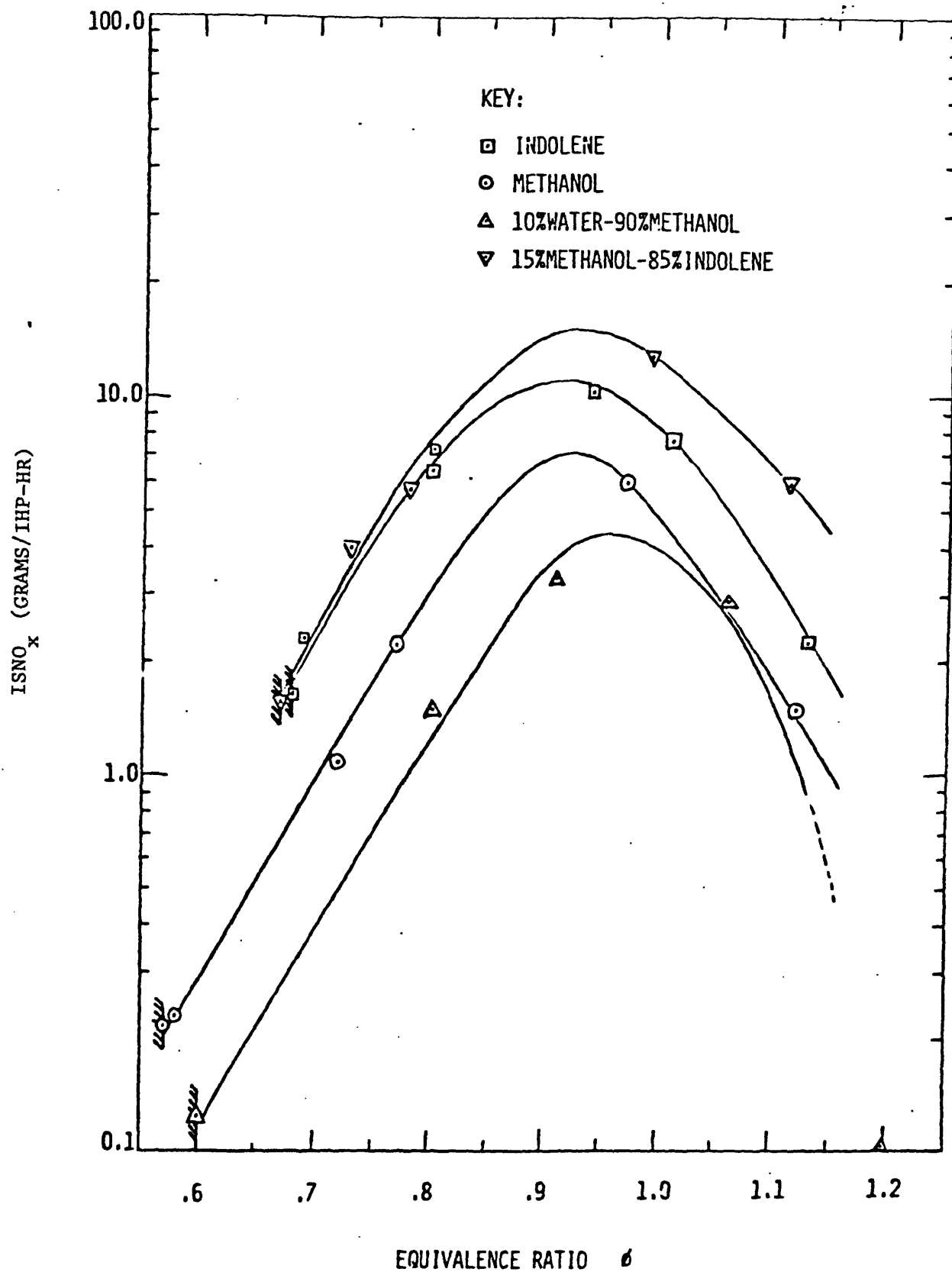


Figure 3 Indicated specific nitric oxide (ISNO_x) vs equivalence ratio (ϕ) and fuel type at baseline conditions

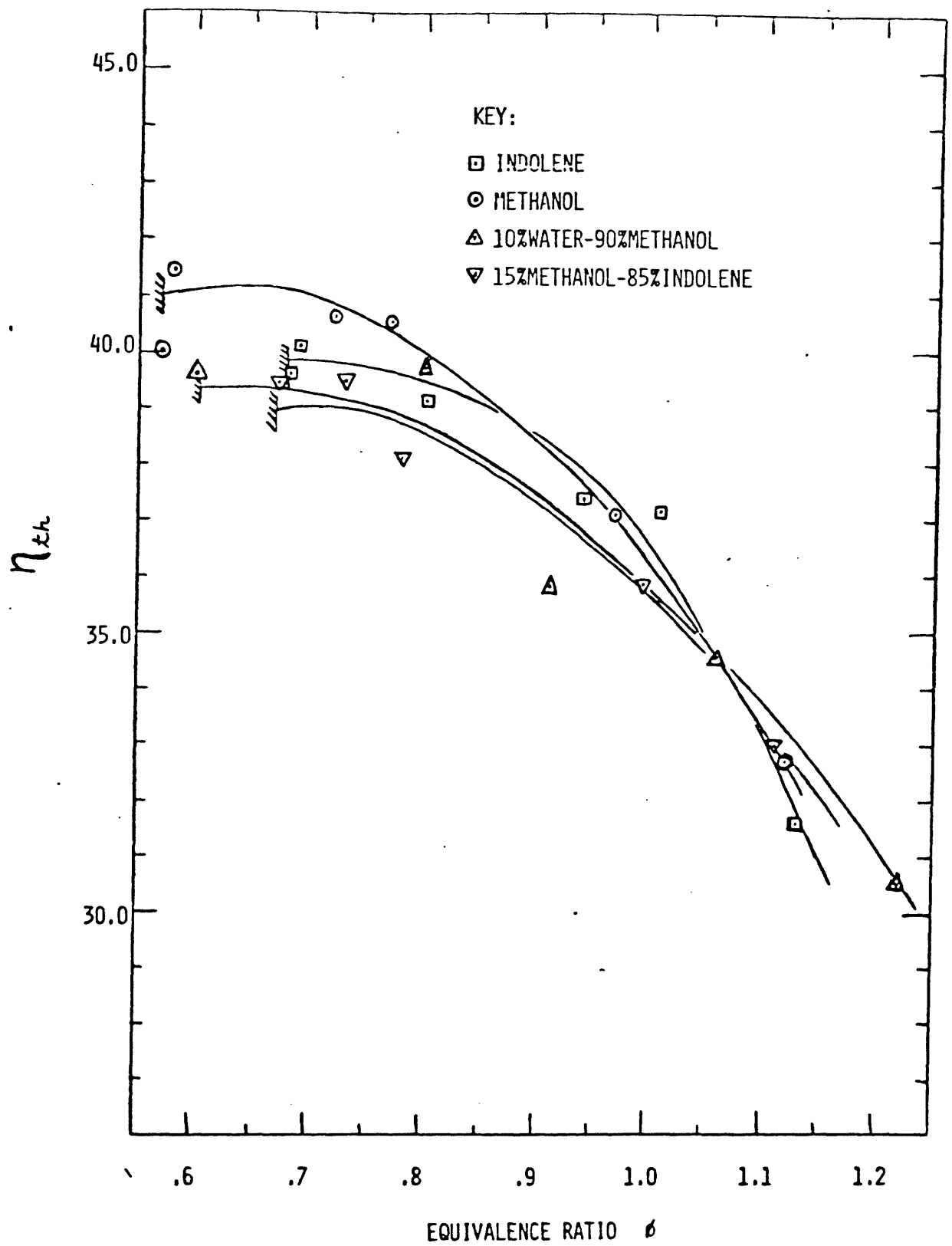


Figure 4 Variation of indicated thermal efficiency (η_{th}) with equivalence ratio (ϕ) and fuel type at baseline conditions

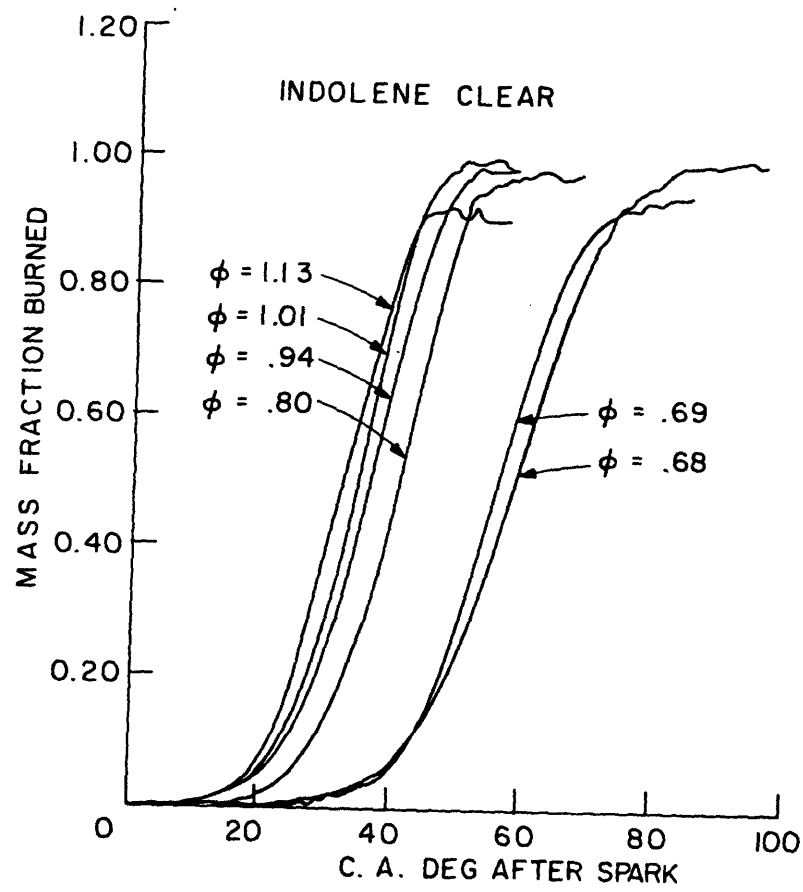


Figure 5 Mass fraction burned vs crank angle for indolene clear

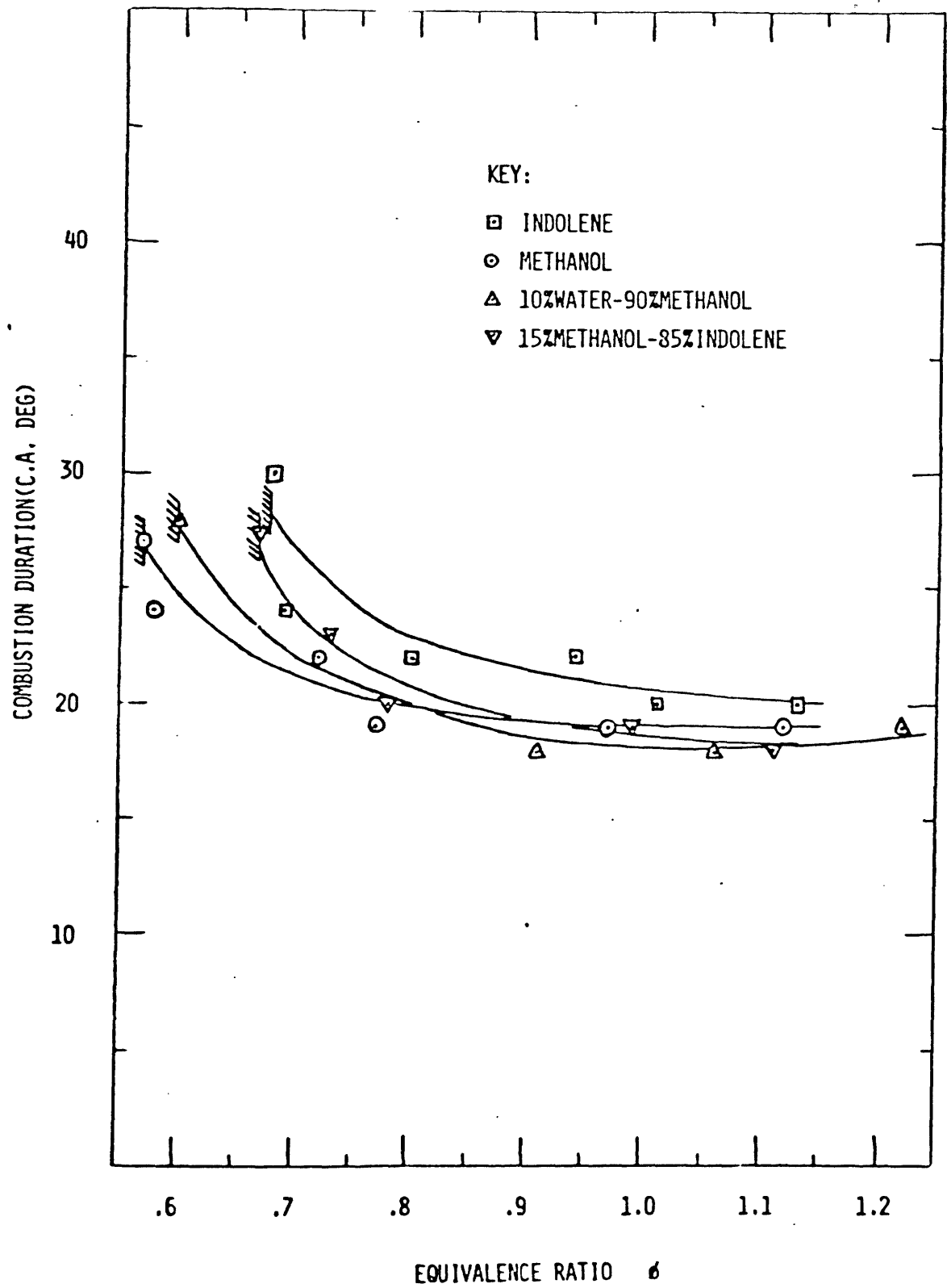


Figure 6 Combustion duration interval (θ_c) vs equivalence ratio (ϕ) and fuel type

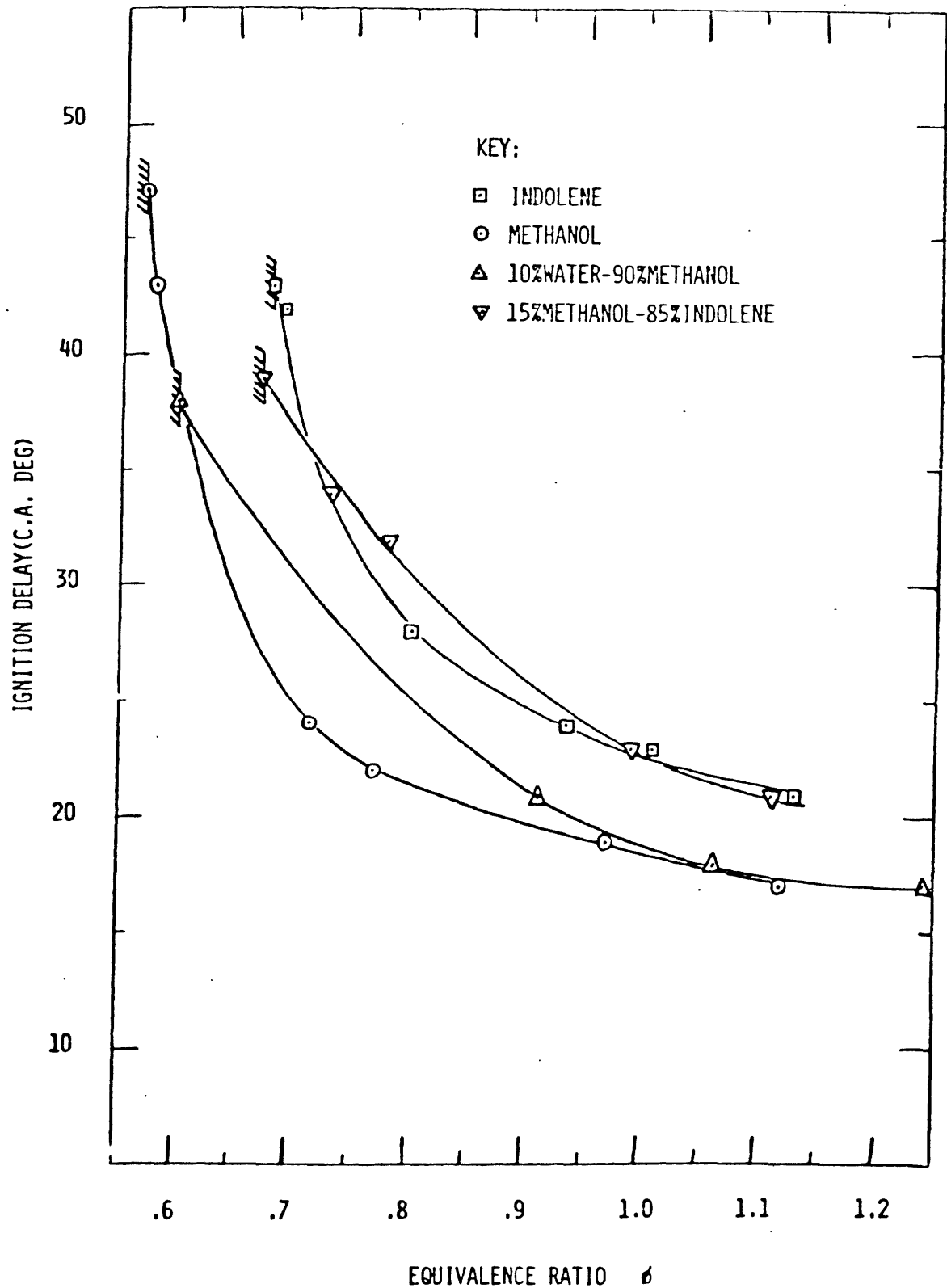


Figure 7 Ignition delay interval (θ_I) vs equivalence ratio (ϕ) and fuel type

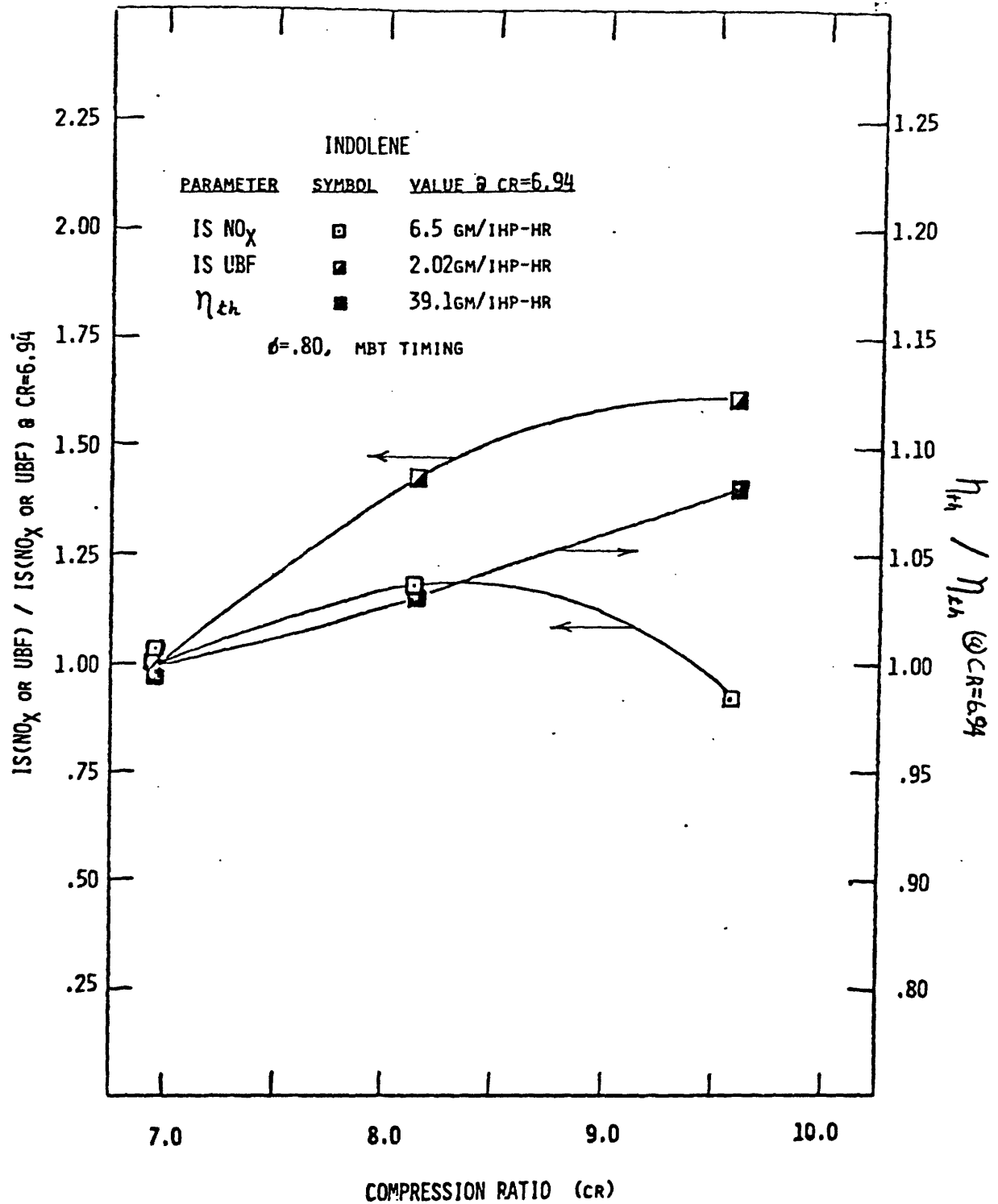


Figure 8 η_{th} , ISNO_x emissions, and ISUBF emissions vs compression ratio (C.R.) for indolene

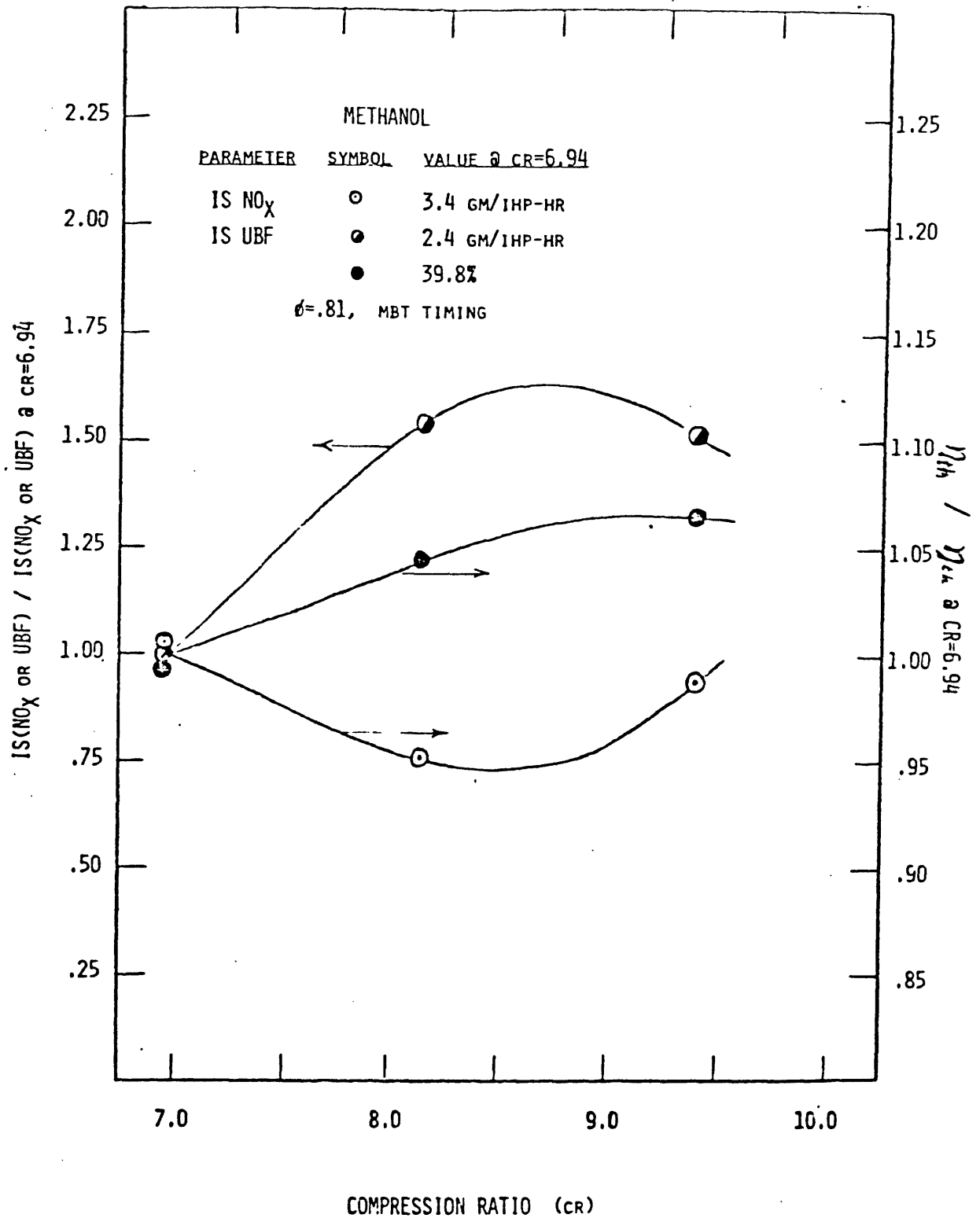


Figure 9 η_{th} , ISNO_x emissions, and ISUBF emissions vs compression ratio (C.R.) for methanol

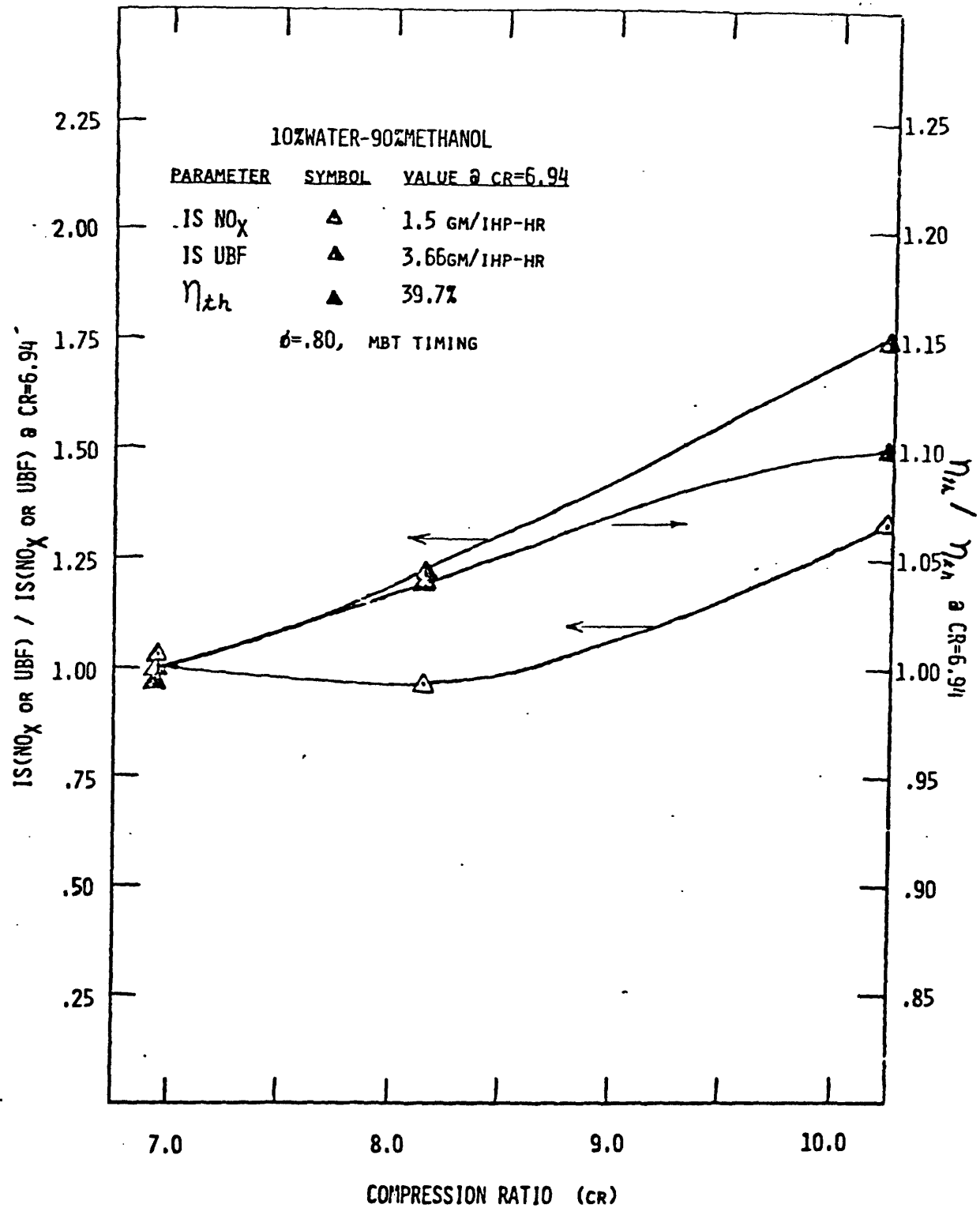


Figure 10 η_{th} , ISNO_x emissions, and ISUBF emissions vs compression ratio (C.R.) for 10% water-90% methanol

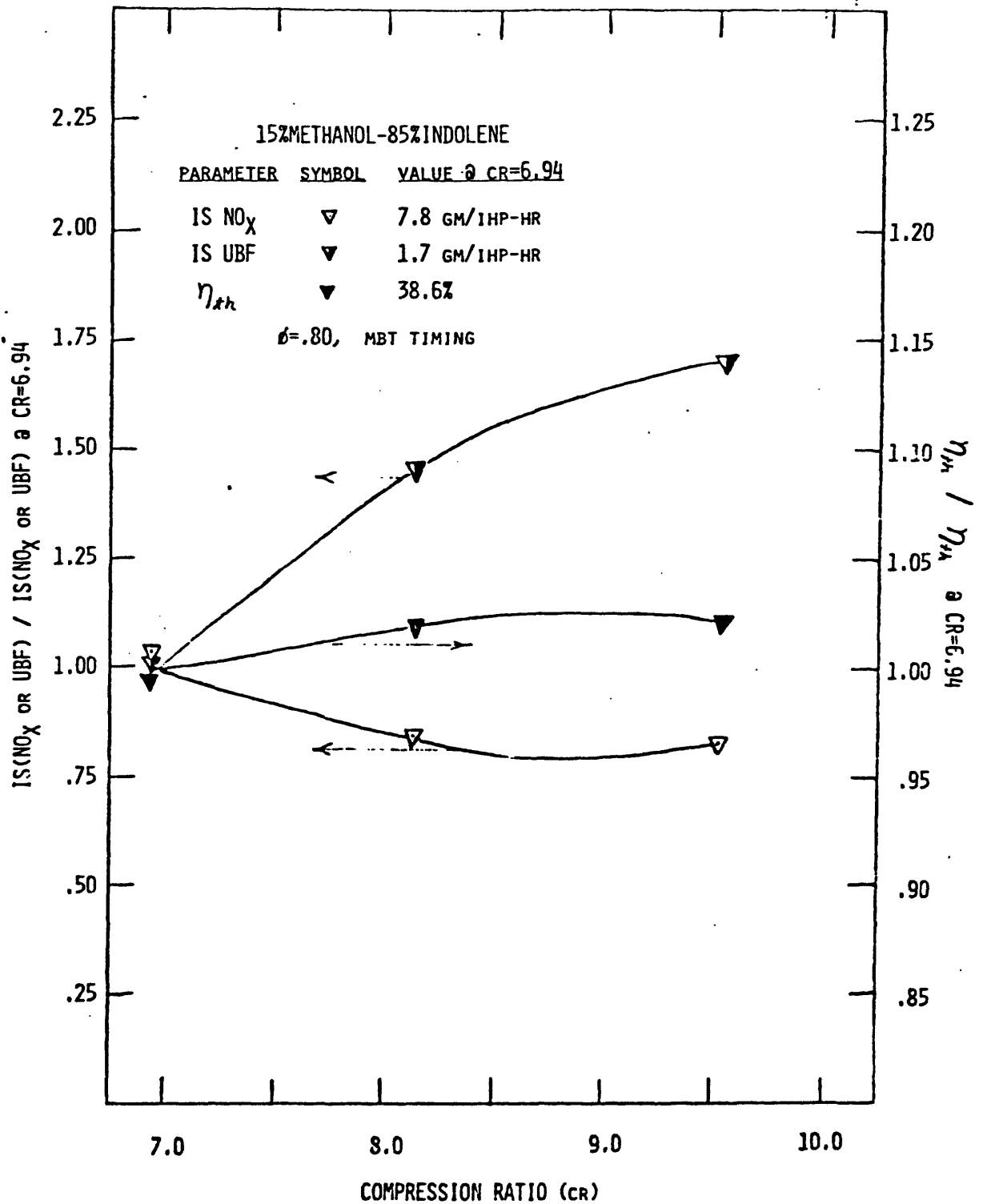


Figure 11 η_{th} , ISNO_x emissions, and ISUBF emissions vs compression ratio (C.R.) for 15% methanol-85% indolene

4. METHANOL-GASOLINE BLENDS: PHYSICAL PROPERTIES

Introduction

Recent changes in cost and supplies of crude oil coupled with growing desire for energy independence in the United States have revived the idea of using methanol as a motor fuel or gasoline extender. In addition to extending the automotive fuel supply a number of other advantages have been claimed for the use of methanol/gasoline blends to fuel automobiles (2-4). Lowered exhaust emissions, increased blended octane values, increased thermal efficiency, i.e. more miles per unit of energy consumed, have all been reported. Unfortunately, use of methanol/gasoline blends in present day automotive engines poses some severe problems, as well, an important one being the stability of the fuel against phase separation. Methanol has limited solubility in gasoline at low temperatures (below about 0°C). Furthermore trace amounts of water have a dramatic effect on phase stability, causing separation into organic and polar (methanol/water) phases, except at elevated temperatures (greater than 40-50°C). Another problem is posed by the positive deviation from Raoult's Law exhibited by the blends. The enhanced vapor pressure of methanol/gasoline blends could lead to problems of vapor lock for certain mixtures at high temperatures.

In the program supported in part with Hawley funds we focused specifically on the phase stability characteristics of methanol/gasoline/water blends. Included were the effects that certain solubilizing "agents" have on the solubility limits of the polar materials. Our approach was to attempt to understand the complex solubility behavior in this system along the way to finding a solution to the phase stability problem.

Results and Discussion

The limited solubility at low temperatures of methanol in gasoline is illustrated in Figure 1, which gives the separation temperature (or cloud point) for varying amounts of methanol in gasoline in the absence of water. (All experiments for this study, unless otherwise noted, were

performed with one no-lead summer formula gasoline, which will be called Brand A.) The separation temperature is defined as the point of incipient phase separation for the mixture, indicated by the change from a transparent to a cloudy state when lowering the temperature gradually from initial conditions at which a stable phase exists. This cloudiness is the result of the formation of tiny droplets of a second phase.

Phase stability is in actuality an even more severe problem than suggested by these data for the following reason. During the distribution of the fuel from the refinery to the tank in the automobile, the gasoline inevitably comes in contact with and absorbs a certain amount of water. Consider now the situation if the fuel is a mixture of gasoline and methanol. The presence of water in large amounts in the fuel storage tank would cause most of the methanol to be extracted from the fuel, resulting in a two-phase equilibrium between a polar (methanol/water) layer and an organic phase which would be largely pure gasoline. This phase separation can be illustrated on the ternary diagram for the methanol/gasoline/water system we recorded in the present study. This is shown in Figure 2. The region of interest in this study is near the methanol-gasoline axis, i.e., at small water content. The approximate tie line representing the separation of methanol/gasoline blends in an underground storage tank is shown along the line connecting points A, B and C. Also shown are a number of other tie lines determined in our study. Point A represents the overall composition of the mixture in the underground storage tank at the gas station (e.g., a mixture of 75% gasoline and 25% methanol as the fuel in a tank containing a certain amount of water). Point B represents the composition of the polar layer, now containing most of the methanol. Point C represents the composition of the fuel. As can be seen, the fuel would be largely gasoline, containing 20% or less of the initial methanol present (i.e., about 5% by volume or less of the fuel layer). Since the region of interest in this study is so compressed on the ternary diagram the more convenient approach of Figure 1 above will be used subsequently to illustrate phase stability in methanol/gasoline/water mixtures.

The separation temperatures for various methanol/gasoline/water mixtures are shown in Figure 3. It is apparent that as the temperature is decreased the tolerance for water decreases. For a fixed temperature an increase in the methanol content of the mixture also increases the tolerance for water, at least for the range of water contents studied here. We should emphasize, however, that for this particular brand of gasoline the addition of methanol will lower the tolerance for water at water concentrations something less than 500 ppm (less than .05%). This can be inferred from the observation that the 0% water line is the asymptotic value for the other water concentration curves.

A number of solubilizers were studied in an attempt to increase the solubility of water in the mixtures. These solubilizers can be broadly classified into three groups, aromatics, aromatic alcohols and higher aliphatic alcohols. In Figure 4A we illustrate the separation temperatures recorded for addition of 5% by volume of a number of solubilizers in methanol/gasoline/water mixtures. With fixed water concentration of 1000 ppm and varying methanol content, addition of aromatics such as benzene and toluene does not increase water tolerance significantly. The presence of 5% benzyl alcohol in the mixture can be seen to eliminate the problem of phase separation down to temperatures as low as 0°C. Tertiarybutyl alcohol is by far the most effective of the additives tested. The effect of addition of solubilizers for higher water contents is illustrated in Figure 4B which is a similar plot for mixtures containing 3000 ppm of water. Again it can be seen that benzene and toluene do not show significant effects, and that benzyl alcohol and tertiarybutyl alcohol are again more efficient in lowering separation temperatures. But separation temperatures can be seen to be higher than for the lower water content of 1000 ppm.

Since the purpose of addition of solubilizing agents is the improvement of the stability of the mixture and since solubilizers are expensive and may affect the combustion properties of the fuel, it is desirable to minimize the amount of solubilizer added. In order to determine the effect of the amount of solubilizer we varied the content of benzyl alcohol in a mixture containing 15% methanol at three different water

concentrations. In brief, the results showed that for concentrations of water of 1000 ppm the addition of 3-4% benzyl alcohol would be sufficient to maintain phase stability above 0°C. In Figure 5 we show the effect of increasing amounts of the solubilizer t-butyl alcohol upon separation temperatures for a 15% methanol blend in gasoline over a range of water content. A notable difference in the solubilizing power of t-butyl alcohol as compared to benzyl alcohol is that separation temperatures continue to reduce proportionately with increasing amount of t-butyl alcohol added, while the effect leveled off for benzyl alcohol. A methanol/gasoline blend containing 1000 ppm water could be maintained stable against phase separation down to 0°C with addition of only about 2% t-butyl alcohol and down to -25°C with addition of about 5% t-butyl alcohol.

There are striking differences in the tolerance of various commercial gasolines for pure methanol in the absence of water. For example, for the range of methanol content of interest (10-20%) the separation temperatures for Brand A are 20°C above those of another gasoline, Brand B. Others (5) report even wider variations for commercial gasolines obtained in the southwest. The separation temperatures for methanol/commercial gasoline blends in the presence of traces of water also vary from brand-to-brand, as might be expected. This is shown in Figure 6 for Brands A and B at two different water contents, 0.1% and 0.3%.

The question now arises as to whether added solubilizer will proportionately further reduce separation temperatures from brand-to-brand for blends in the presence of traces of water. In Figure 7A we show these data for the two commercial brands already discussed and added benzyl alcohol at 5% as solubilizer. Brand B, which already had a high methanol/water solubilizing tendency, was enhanced as a solvent even more than Brand A, which had a lower solubilizing tendency. It is interesting to note that Brand B without solubilizer is stable to lower temperatures than Brand A with 5% solubilizer added.

Finally, we considered briefly the question of the acceptability of methanol/gasoline blends as fuels for present internal combustion engines. This topic has been considered elsewhere (1,3,4) and was

not within the scope of our experimental studies. We have, nonetheless, recorded the ASTM distillation curves over the entire range of methanol content and in the presence of traces of water. These data are shown in Figure 8 for methanol content in Brand A ranging from 0 to 100% in the absence of water. In addition we found for the case of 20% methanol content and 0.2% water in Brand A that even this relatively high amount of water does not affect the distillation curve significantly. Finally, Reid vapor pressures (RVP) were recorded for blends of Brand A with methanol over the entire range of methanol content, as shown in Figure 9.

The vapor lock index (VLI) has been found to be a reliable measure of a methanol/gasoline blend's tendency to give high temperature driveability problems, such as vapor lock (3). The higher the VLI, the greater the tendency to such problems. The VLI for the base fuel, Brand A, and for a 15% methanol blend with Brand A are, respectively, 12.7 and 18.2, where $VLI = RVP + 0.13 \times (\% \text{ distilled at } 70^{\circ}\text{C})$. This substantial increase in VLI suggests that some reblending of the base fuel would be necessary.

CONCLUSION

Among the problems in the use of methanol/gasoline blends as automotive fuels the problem of phase stability is especially important. The tendency for traces of water to cause separation into organic and polar (aqueous) phases at a particular temperature has been shown to be a strong function of methanol content, of water content, of gasoline composition (brand-to-brand comparison), and of added solubilizer for methanol/water. In general it is possible to find solubilizers which enhance the solvent power of gasoline for methanol and water, with notable effectiveness having been demonstrated for an aromatic alcohol and a branched aliphatic alcohol. Specifically, for a blend of summer formula gasoline, 15% methanol, and 5% benzyl alcohol as solubilizer, it should be possible to tolerate 3000-4000 ppm water (0.3%-0.4%) in the northeast during the summer without problems of phase separation.

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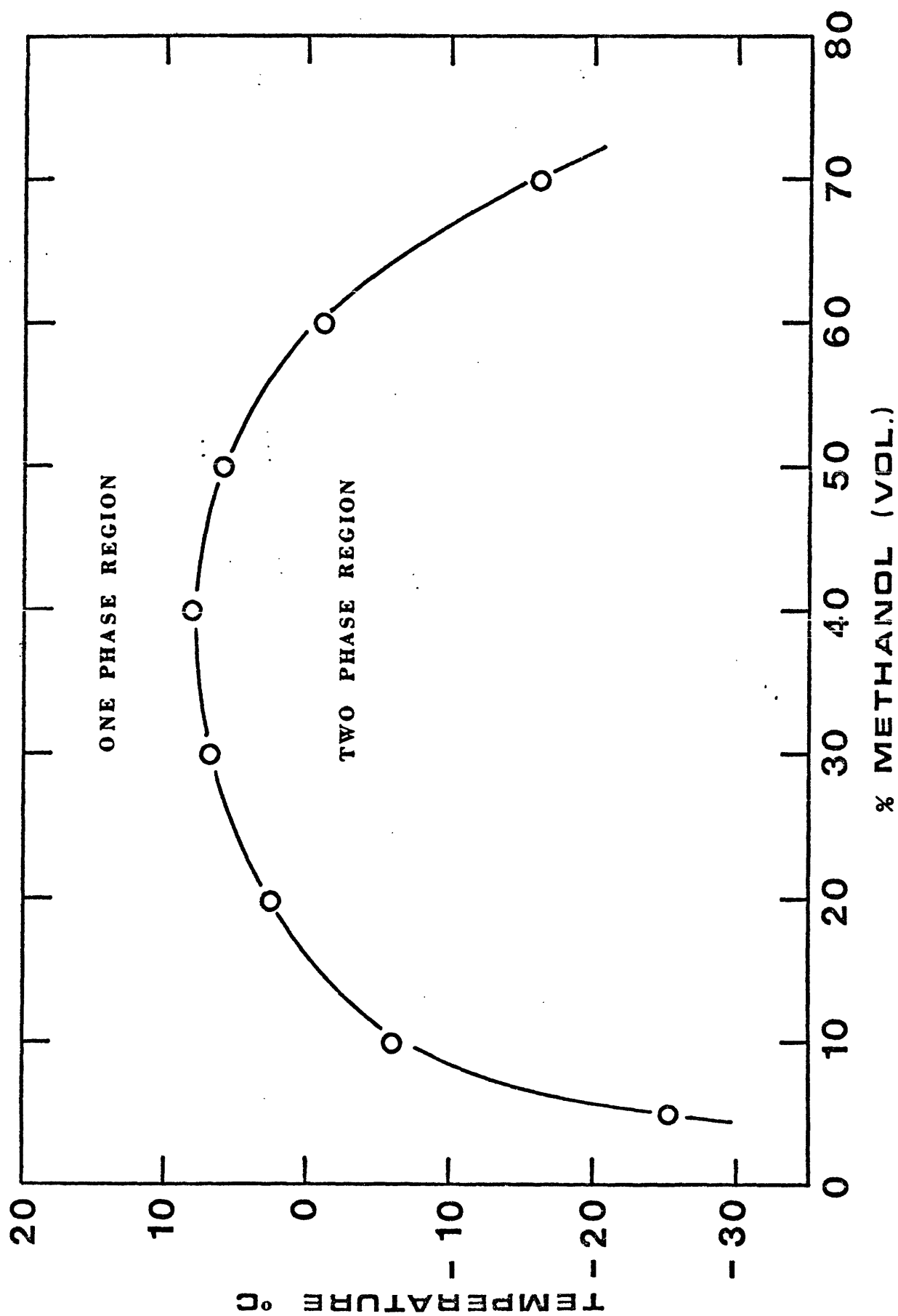


Figure 1. - PHASE SEPARATION TEMPERATURE FOR METHANOL/GASOLINE BLENDS

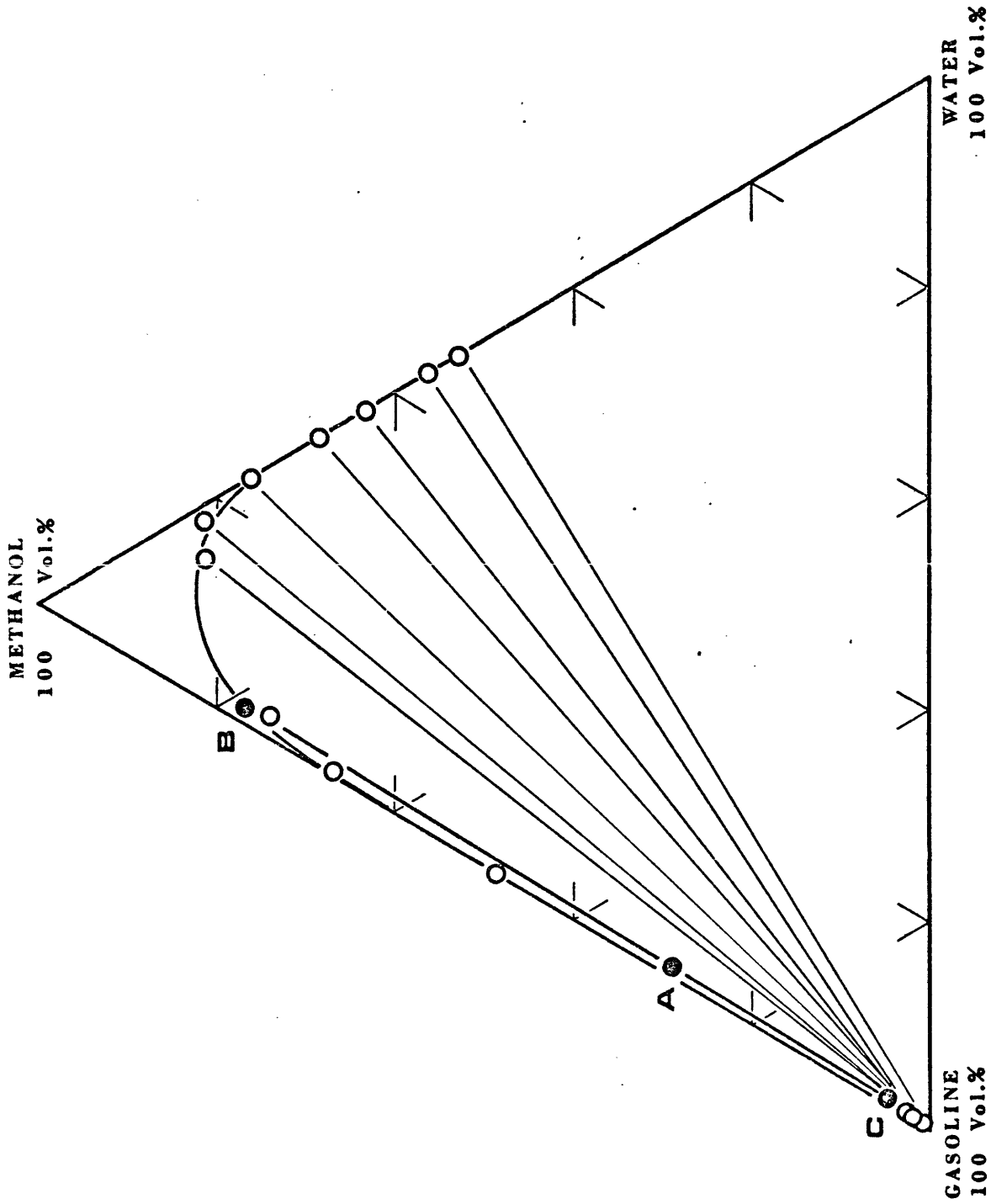


Figure 2. - PHASE DIAGRAM FOR METHANOL-GASOLINE-WATER MIXTURES AT 20° C

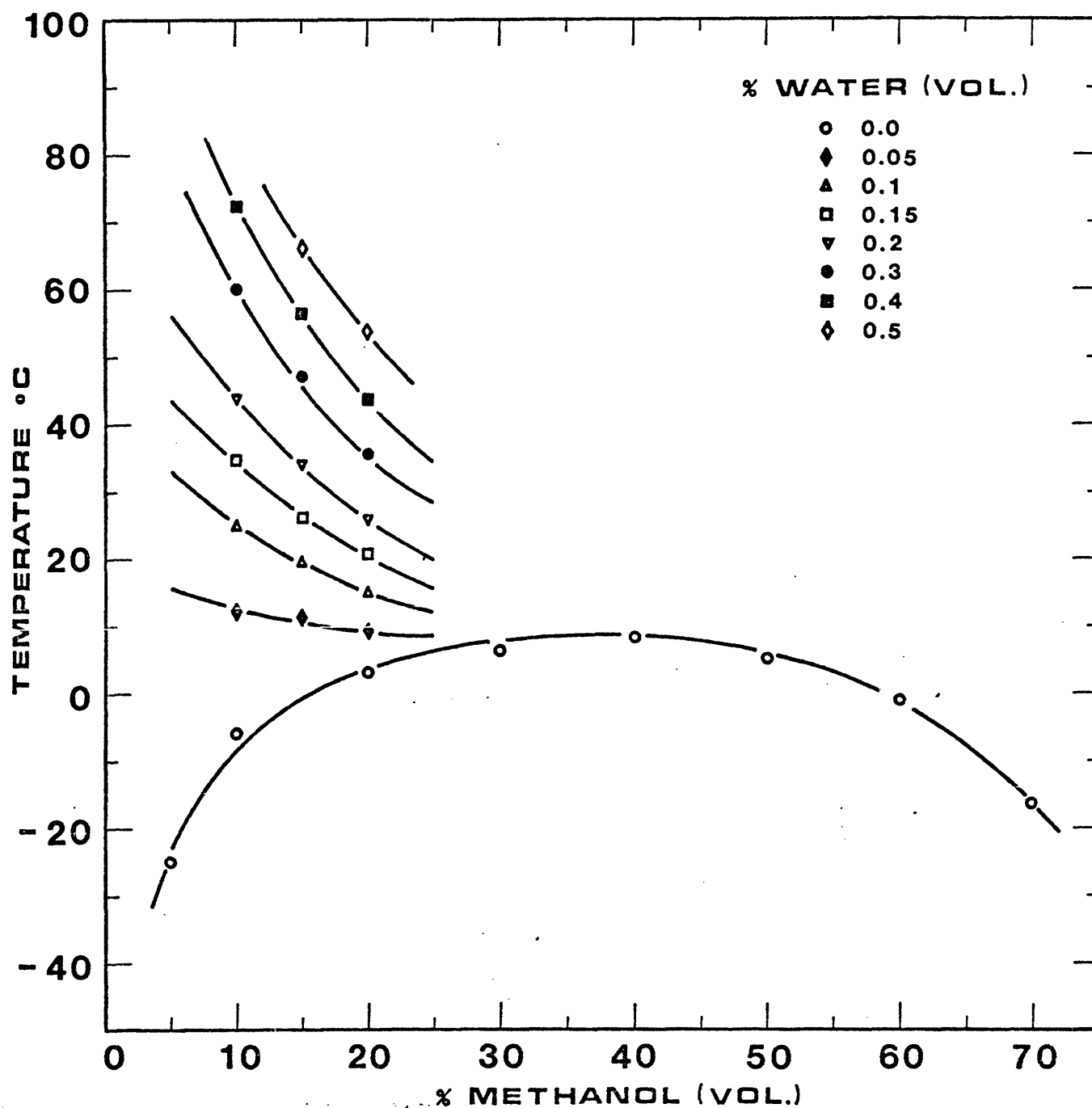


Figure 3. - PHASE SEPARATION TEMPERATURE FOR A METHANOL/GASOLINE BLEND IN THE PRESENCE OF SMALL AMOUNTS OF WATER

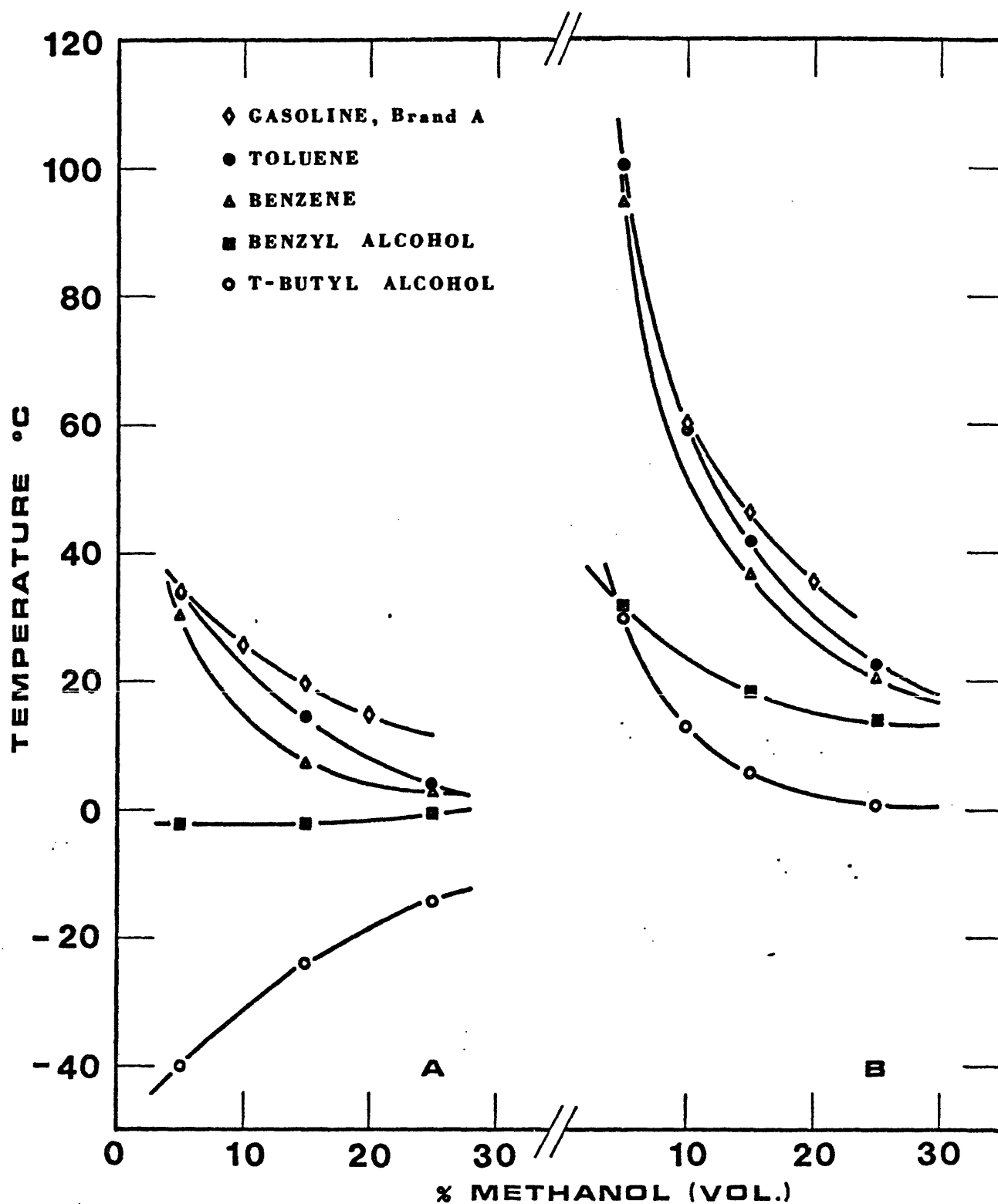


Figure 4. - EFFECT OF SOLUBILIZING AGENTS ON THE PHASE SEPARATION TEMPERATURE OF METHANOL/GASOLINE BLENDS CONTAINING A) 1000 PPM , B) 3000 PPM OF WATER

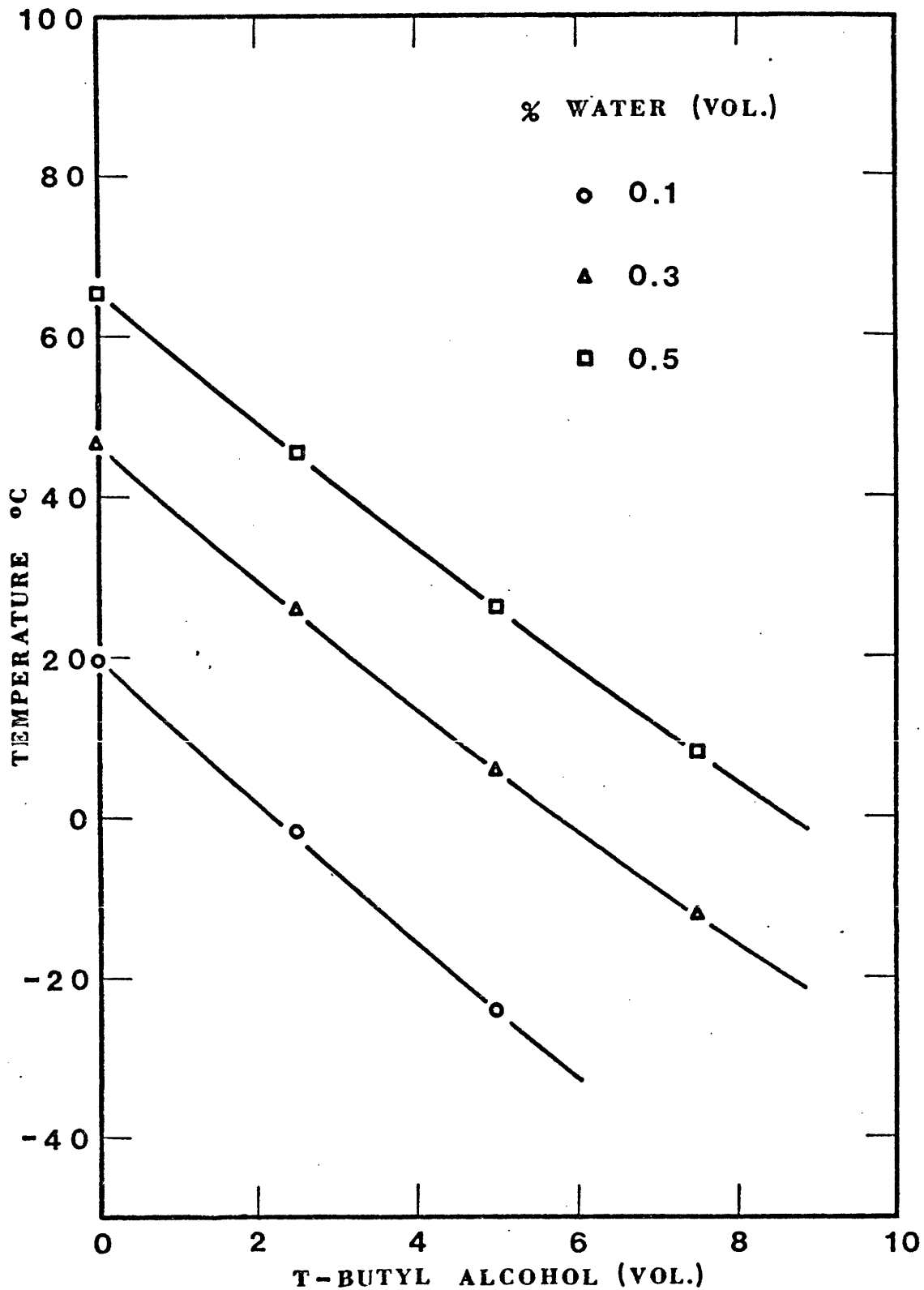


Figure 5. - EFFECT OF THE AMOUNT OF T-BUTYL ALCOHOL ON THE PHASE SEPARATION TEMPERATURE OF A 15% METHANOL/GASOLINE BLEND FOR VARIOUS CONCENTRATIONS OF WATER

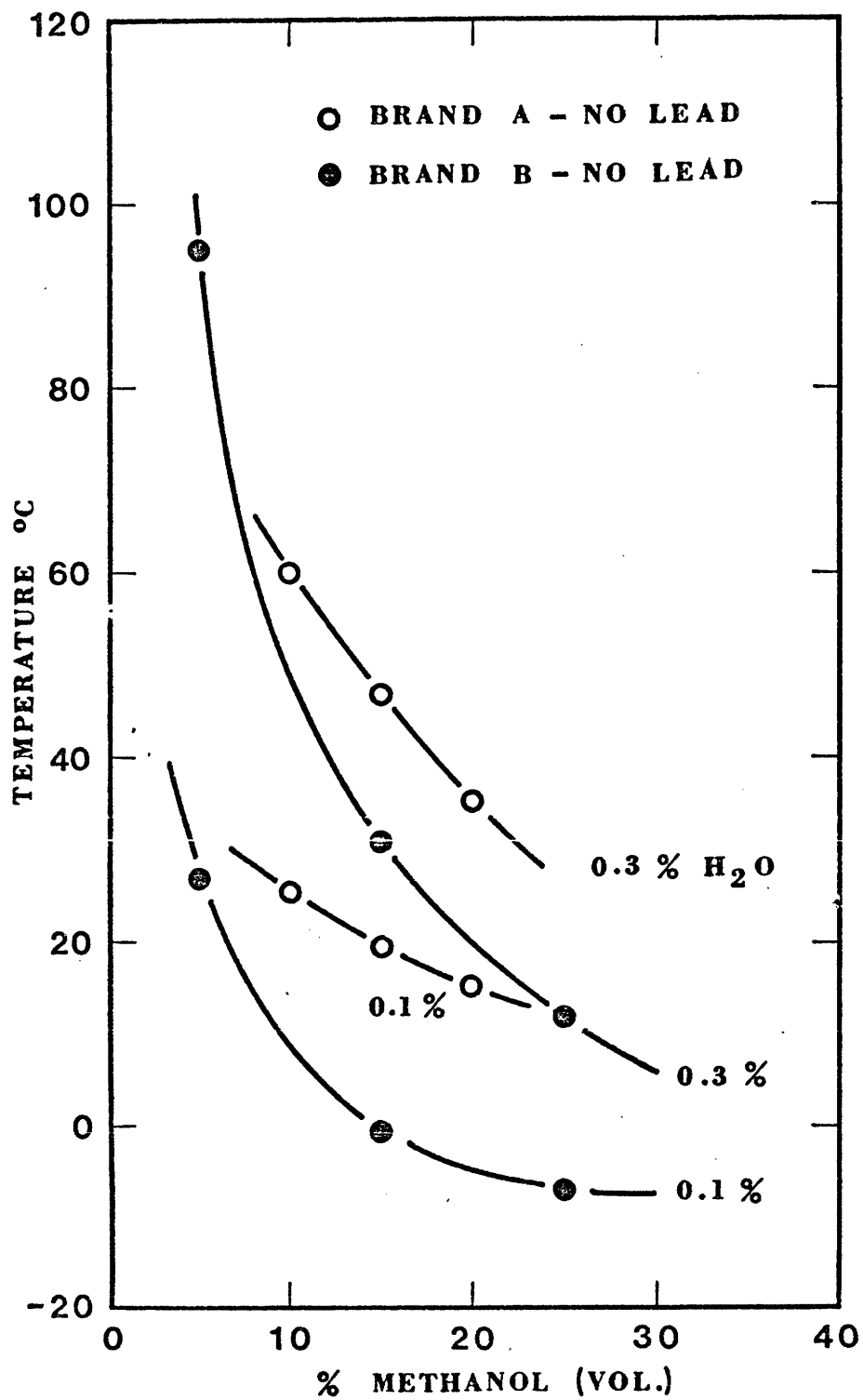


Figure 6. - VARIATION IN PHASE SEPARATION TEMPERATURE FOR BLENDS OF METHANOL AND TWO DIFFERENT BRANDS OF GASOLINE IN THE PRESENCE OF WATER

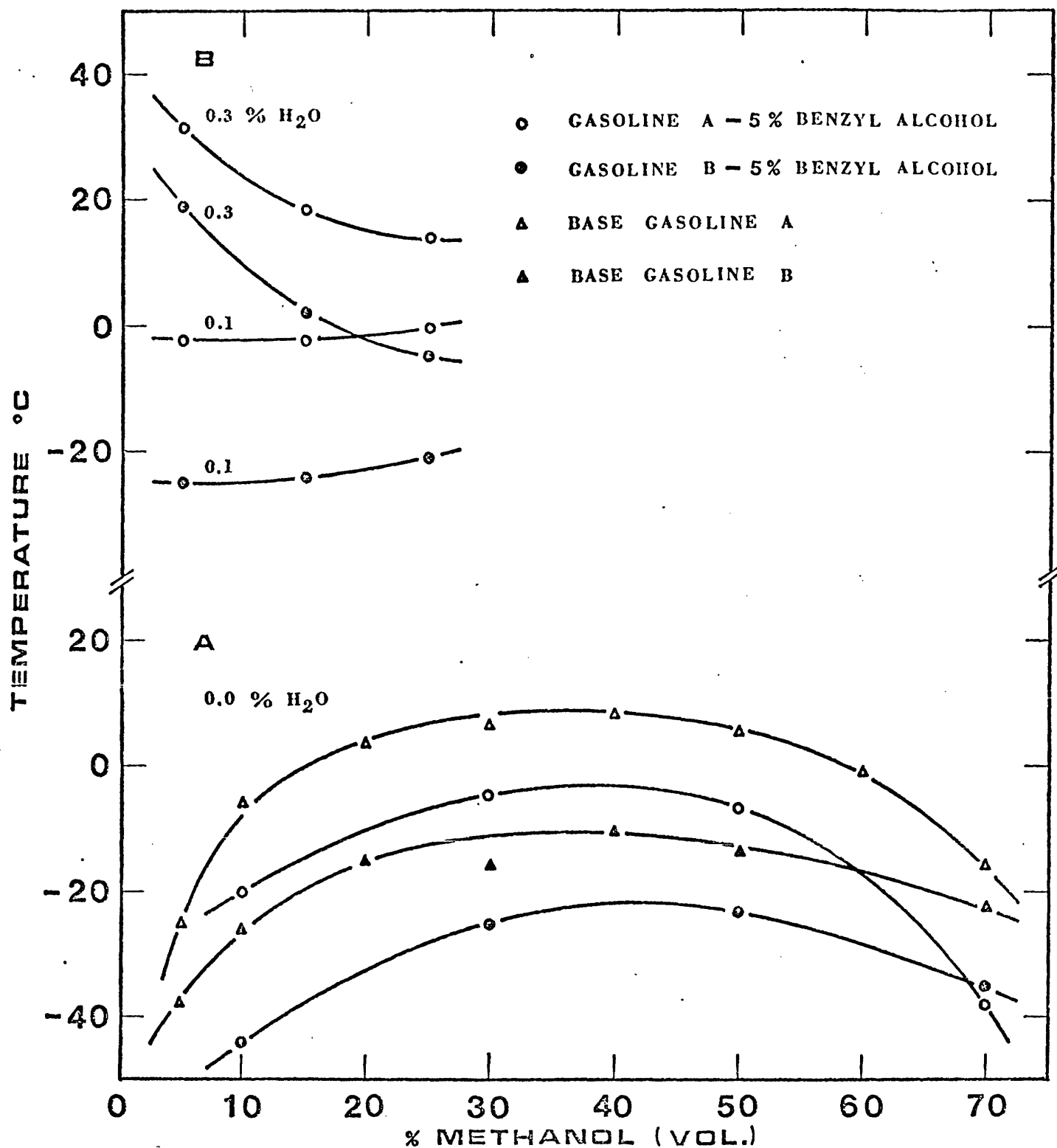


Figure 7. - VARIATION IN PHASE SEPARATION TEMPERATURE FOR BLENDS OF METHANOL AND DIFFERENT BRANDS OF GASOLINE IN THE PRESENCE OF 5% BENZYL ALCOHOL A) IN THE ABSENCE OF WATER, B) WITH SMALL AMOUNTS OF WATER

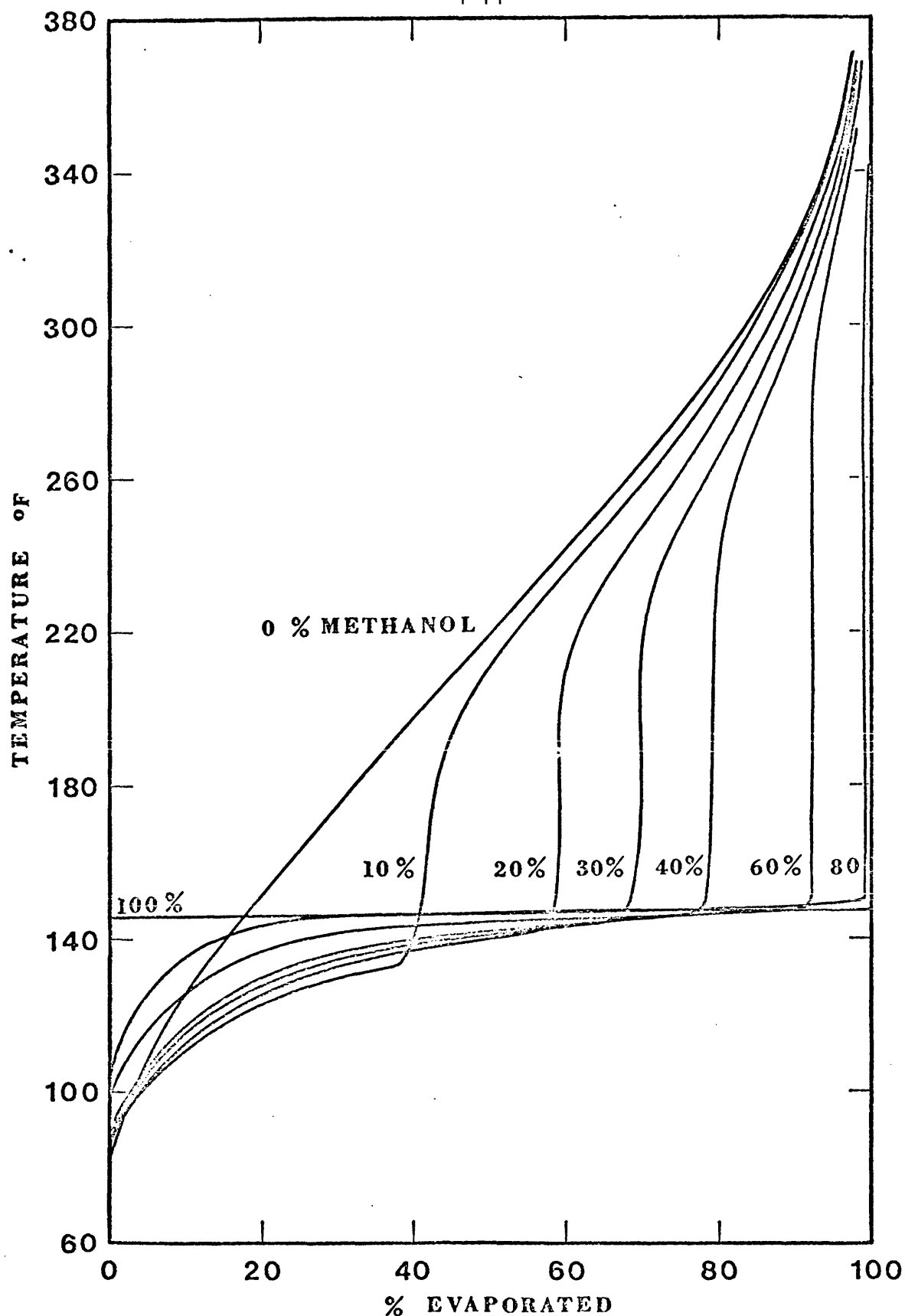


Figure 8. - ASTM DISTILLATION CURVES FOR METHANOL/
GASOLINE BLENDS

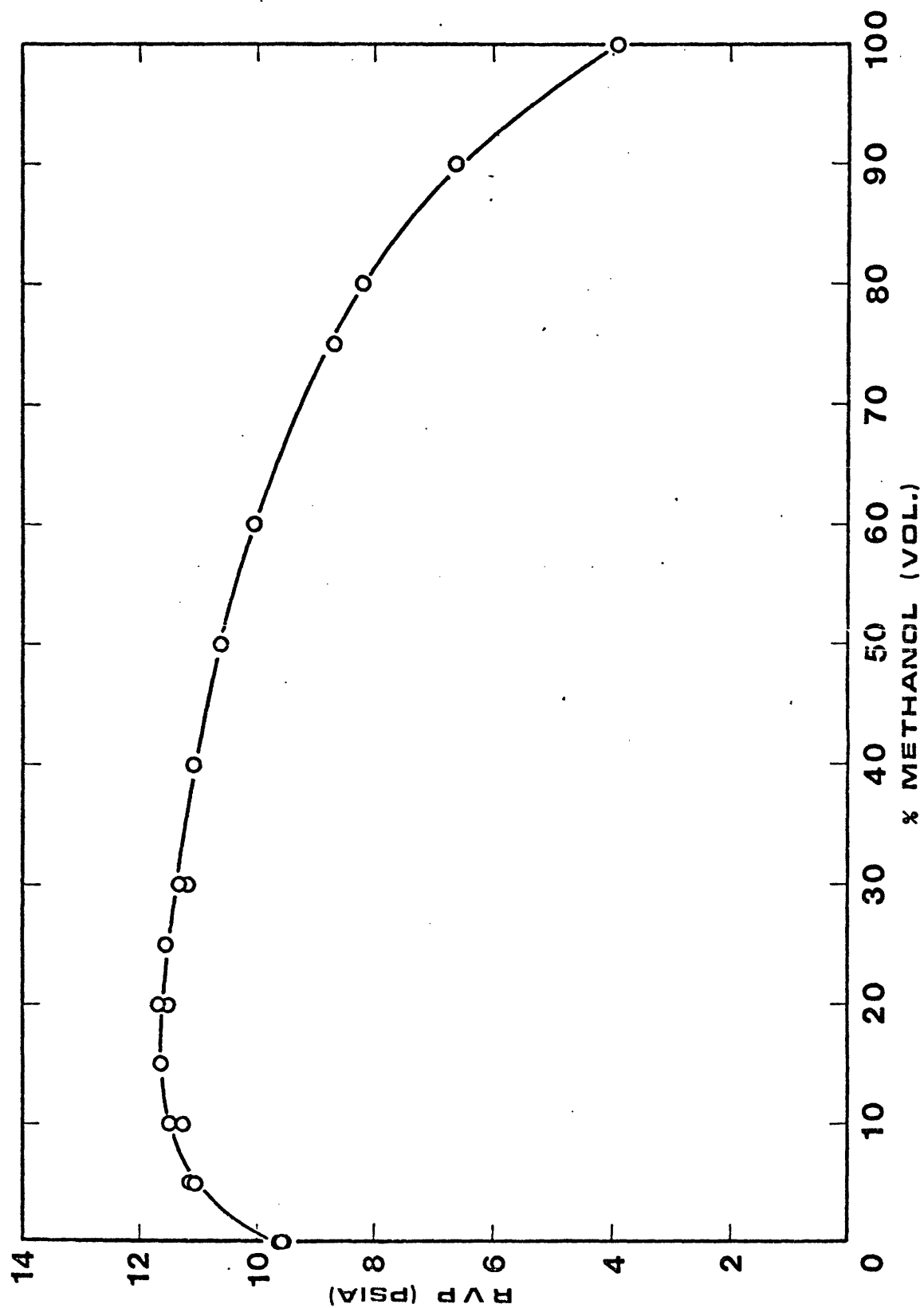


Figure 9. - ASTM REID VAPOR PRESSURE FOR METHANOL/GASOLINE BLENDS

5. METHANOL INFORMATION ACTIVITIES

Methanol Information Center:

During the period March 1974 - June 1975, the methanol group of the Energy Laboratory received a large number of inquiries on the use and the production of methanol as a synthetic fuel. These inquiries ranged from elementary and straightforward ones, to serious questions from groups planning to construct plants and looking for cost estimates. In an effort to answer as many as possible of these questions, a number of publications were written as meeting speeches or journal articles (see the attached list). A series of information sheets were prepared for circulation, which gave recent developments in this fast-moving field. In most cases this type of information satisfactorily responded to the inquirer's needs, but in some cases, letters, telephone calls and sometimes visits followed. Dr. T.B. Reed testified before Congressional Committee hearings three times - the Proxmire Appropriation Committee, the McCormack Energy Committee and the Republican House Energy Subcommittee. Dr. Reed also gave a number of talks at scientific meetings.

In certain instances there appeared to be special opportunities for short-term action which could result in methanol becoming available as a fuel, and in some of these cases the questions were as much financial as technical. For this reason an industrial consultant, Mr. W.A. Stevenson, was retained who helped in making preliminary cost estimates for methanol production. At one time the Massachusetts Port Authority was seriously

interested in converting Boston municipal waste to methanol in a plant similar to that now being constructed by Seattle. Relevant information was supplied. The Lowell Gas Company and Dutchess County Waste Commission is also interested in synthetic liquid and gaseous fuels from waste and may be proceeding on the basis of our initial information.

Early in 1974 we were contacted by the EPA to undertake a methanol evaluation program and were assured that they had funds on hand. They said that many other people were talking about doing methanol research, but they wanted to support the M.I.T. Energy Laboratory because we had begun a modest program under the Hawley grant and had started basic work under Professors Donnelly and Heywood. We wrote several proposals for work in the areas of their interest but for a variety of reasons these have not yet been funded.

Biomass Conversion to Synthetic Fuels:

An advantage of methanol as a fuel is that it can be made from coal using existing technology, and interest in this was shown in the Project Independence Report, "Methanol From Coal for the Automotive Market," (Jaffee, et al.). Other gaseous and liquid fuels can also be produced from biomass. However, it soon became apparent that another very attractive source for methanol was municipal waste, since most municipalities are now paying in excess of \$10/ton to dispose of it. Though capital costs would be higher than coal conversion, this is roughly compensated for by the lower fuel costs. We described this option to the City of Seattle engineers early in 1974, and they are now proceeding to build a

1500 ton/day plant. At present it looks as if they will produce ammonia rather than methanol, but the processes are almost identical and the options are still open.

Although wood (and farm wastes) will never be as cheap a source of methanol as municipal waste, they have the potential for supplying much larger volumes. Therefore we made preliminary estimates of the cost of converting wood to methanol, using figures based on the AEC and Seattle studies. These were presented at the National Pulp and Paper Meeting in Syracuse in June 1975, and a great deal of interest has arisen in the wood community as a result.

In initial projections of energy sources for the country, biomass and wood were totally ignored (except by Hottel and Howard of M.I.T.) or dismissed in a few lines. More recently ERDA has become interested in the potential of biomass in making synthetic fuels, and there are presently several studies under way looking at these sources.

METHANOL PUBLICATIONS FROM THE MIT ENERGY LABORATORY

1. "Methanol: A versatile Fuel for Immediate Use," T. B. Reed and R. M. Lerner, *Science* 182, 1299 (1973). This article gives an overview of the many uses of methanol as a synthetic fuel, especially automotive, and the many sources from which methanol can be manufactured. It describes the possibility of methanol production from municipal waste, a process that is now being developed by the City of Seattle.
2. "Improved Performance of Internal Combustion Engines Using 5-30% methanol in Gasoline," T. B. Reed, R. M. Lerner, E. D. Hinkley and R. E. Fahey, Paper 749104 at the Intersociety Energy Conversion Engineering Conference, Aug. 1974, p. 952 in proceedings. This paper presents data on ten randomly selected cars using methanol and shows generally increased fuel economy, lowered emissions and improved antiknock for mixtures up to 15%.
3. "Sources and Methods for Methanol Production," T. B. Reed and R. M. Lerner, published in proceedings of the THEME (Hydrogen) Conference of meeting held March, 1974. This paper reviews all methods of making methanol and gives preliminary economic evaluation of costs.
4. "Methanol for Fuel - A Bibliography on the Production and Use of Alcohols as Fuels," Thomas B. Reed.
5. "Comparison of Methanol and Methanol-Blends," Thomas B. Reed, Proceedings of the Methanol Conference, Heniker N. H., July 1974, Engineering Society. This paper evaluates the merits of burning methanol by itself versus burning it as a blend with gasoline.
6. "Use and Production of Methanol as a Synthetic Fuel," T. B. Reed, Paper submitted to the American Chemical Society for a book, "Energy and the Environment." Evaluates Methanol production methods and costs.
7. "Biomass Energy Refineries for Production of Fuel and Fertilizer," T. B. Reed, to be published in the proceedings of the Eighth Cellulose Conference, May 1975 (TAPPI and SUNY) Syracuse, N. Y. This paper discusses the feasibility of using biomass for energy and outlines the various wet and dry processing methods now available. Production of methanol from coal, waste and wood are discussed in considerable detail using figures developed by the AEC and Seattle for coal and waste.
8. "Methanol Information Sheets, # 1, 2 and 3." T. B. Reed. These sheets have been prepared to answer questions most often asked in the hundreds of letters we receive on the subject of methanol, and to give latest news of events in this rapidly changing field.

6. DEVELOPMENT OF A METHANOL BLEND FLEET TEST PROGRAM

Program Goals

The purpose of the Methanol Blend Fleet Test was to determine the feasibility of utilizing approximately a 10% blend of methanol with gasoline as an automotive full extender for vehicles normally expected to be operating on the American roads between 1975 and 1980. The goals of the program as initially laid down by the Program's principal investigator were to evaluate the following aspects of methanol blend use, relative to conventional gasoline use:

1. Vehicle driveability
2. Vehicle fuel economy
3. Fuel anti-knock characteristics
4. Vehicle materials compatability (especially the fuel system)
5. Water contamination and phase separation in vehicle fuel and fuel storage systems
6. Public acceptance of methanol blends
7. The practicality of using methyl-fuel with blends to improve tolerance to water induced phase separation.

It was proposed to use a fleet of cars owned by members of the M.I.T. community for the program. The size of the fleet was to be 200 vehicles distributed as indicated in Fig. 1.

A search of automotive literature available in the public domain revealed that there were no universally acceptable standards for methods of fuel preparation, test conditions, measurement techniques and other

parameters for evaluating methanol-gasoline blends in fleet tests. Past research has been concentrated on ethanol-gasoline blends and is over 40 years old and was performed on vehicles which are now obsolete. Much of the more recent pertinent information has not yet reached the public domain. At several conferences ⁽¹⁾ held this past year on the use of methanol as an alternate fuel, it was found that results obtained in different vehicle tests with methanol blends easily be related to another because of a lack of standards in test methods (see Fig. 2). The conferees also recommended that a workshop be sponsored through appropriate agencies to establish acceptable standards for fleet testing of methanol-gasoline blends.

Fleet testing generally implies the testing of like models and years with similar engines. The proposed M.I.T. Fleet would be a wide diversification of vehicles, models, years and engines and would therefore not categorically fit any prescribed "fleet test" methodology. There were no standard tests available that were technically acceptable to all sectors of the automotive community. A trial innovative methodology would have to be devised, the results of which could then be used as a partial base to further ascertain a standard method for fleet testing of fuel blends when investigated by an appropriate body of concerned automotive organizations.

Given these difficulties, it became clear that a reexamination of the initial goals of the program was called for, and this process was started by program personnel in late 1974. It was evident that the original

goals of the M.I.T. Fleet Test Program were both broad and complex. This reexamination of program goals established that studying anti-knock behavior would be extremely difficult in a fleet test, was better suited to an investigation in a laboratory research engine program, and was beyond the scope of the M.I.T. Fleet Program. In addition, vehicle materials compatibility studies would be extremely costly in time, personnel, and funding. These were, therefore, dropped from serious consideration, although any data observed that was obviously connected with materials deterioration due to methanol use would be documented. Determination of public acceptance or non acceptance was also to be eliminated, since it was felt that the program should not assume the role of public poll-taking.

The practicality of adding a small percentage of methyl-fuel to the methanol-gasoline blends in order to improve tolerance to water induced phase separation was combined with the study of separation of methanol from blends.

As a consequence of this reexamination of goals, the redesigned Fleet Test Program would concentrate on the following aspects of methanol-gasoline blend as

1. Vehicle driveability
2. Vehicle fuel economy
3. Water contamination and methanol-gasoline phase separation problems

These tests would be conducted through hot and cold seasonal weather changes.

Fleet Methodology and Test Procedures

Two different approaches were proposed to obtain data from the fleet vehicles. A selected representative group of vehicles would be tested extensively using special test procedures and instrumentation. And, the entire fleet would be operated over an extended period using methanol-gasoline blend fuels; reports from vehicle owners would constitute the data base for this part of the fleet test program.

For the smaller selected group of vehicles, a set of test methods acceptable to the widest number of members of the automotive community was decided upon; these were a modified series of Coordinating Research Council (CRC)⁽²⁾ tests. These CRC test techniques were designed to evaluate the problem areas of vapor lock, hot start and run, and traffic driveway. (See Appendix A for vapor lock/driveability terminology).

Driveability is a term that implies acceptable operation of a vehicle in a number of different fuel problem areas such as:

1. Cold start (after overnight soak)
2. Hot start and run
3. Vapor lock
4. Traffic driveway

These CRC type tests evaluate driveability in terms of fuel volatility. Evaluation of incipient vapor lock, which is one of the more critical driveability concerns was to be a priority study. An impending vapor locking situation is determined when a limiting volatility is reached, namely, the temperature at 20 V/L⁽³⁾ (vapor to liquid volume ratio adjusted to the reference temperature) of a fuel which causes a 25% increase

in acceleration time. Blends would be varied to bracket this limiting volatility. Test runs for the operation of a car throughout a prescribed sequence of operating conditions or maneuvers for a single test fuel are conducted. Reid Vapor Pressures (RVP)⁽⁴⁾ are taken from fuel samples and are converted to an equivalent temperature at 20 V/L, are adjusted for deviation of ambient temperature and then plotted against the percent increase in car acceleration time. From these plots, the most critical speed range and limiting temperature at 20 V/L are determined for a 25% increase in acceleration time. Variations of the percentage of methanol to a given base stock of gasoline will give the vapor locking tendency of the blend.

A demerit system for scoring results would be assigned to all malfunctions observed during a test run. Demerits are plotted as a function of RVP, which is used as an indicator of fuel volatility within a fuel series.

Fuel economy test runs were to be made by a standard precision two buret fuel test apparatus over measured distances under different maneuvers. The fuel economy test apparatus was to be connected to the engine on the tank side of the fuel pump, by-passing the vehicle fuel tank supply line.

Driveability tests and fuel economy tests were going to be conducted in three different modes on a number of cars representing a cross section of the fleet. First, on laboratory dynamometer test runs under controlled conditions of temperature, humidity, etc. The joint carrying out of these lab tests was being negotiated with the Scientific Energy Systems Co. of Watertown, Massachusetts which has the required equipment and instrumentation capabilities. They were interested in corroborating with the M.I.T.

Fleet Test Program on the above kinds of tests since they were already doing engine emissions studies for the EPA. Parallel to this kind of effort the Program staff were going to perform similar kinds of tests on actual road and track runs on instrumented cars representing a cross section of the fleet.

For the test program for the entire fleet, the main portion of the fleet was to be split into two groups; a control group of vehicles operating on straight gasoline, and a group periodically alternating on straight gasoline and methanol-gasoline blends. Data on both groups would come from detailed individual vehicle performance reports covering key information such as: fuel economy, frequency of stalls, idle quality, back-fire, hesitation, stumble, stretchiness, surge, quality of starts, starting times and number of restarts.

Data from the smaller selected vehicle fleet tests would cover the same vehicle performance and driveability attributes, but the different throttle positions at which many of these problems occurred would be noted (e.g., throttle positions such as part throttle, wide open throttle, road load, tip in, and crowd: see Appendix A for definitions of terminology).

A faculty member from the M.I.T. Mathematics Department and from the Sloan School of Management agreed to assist in the design of data taking methods, weighting of demerits for data taken, and subsequent data processing and analysis.

Studies of Water Induced Phase Separation

Problems associated with methanol separation from blends at low temperatures due to water contamination problems, and the use of small

amounts of additives such as 1% methyl-fuel to retard or control these processes, were to be investigated in the field, and in laboratory tests on numerous samples of seasonal fuels blended with up to 15% methanol over a temperature range of -40°F to 65°F.

The problem of excessive water accumulation in the Field Test Station fuel storage facilities (Fig. 3) were to be closely monitored by taking water tests of tanks, and by recording relevant data such as weather conditions, ground and tank temperatures, vapor recovery techniques, and fuel handling and dispensing procedures. Water contamination occurring in vehicle fuel distribution systems was to be studied as well. Based on initial methanol-gasoline blends used for preliminary tests on personal vehicles during the months of November, December and January there were no observable problems encountered, although intense investigation in this area was not to commence until later in the winter. Laboratory tests for methanol separation in blends had just started in late January 1975.

Preliminary Preparations for Fleet Test

During the period between October 1974 and late January 1975, there were numerous activities that ran parallel to the design of fleet test methods that were to impinge heavily on the planning of the overall Fleet Test Program. Determination, negotiation, and resolution of associated problems that were important and necessary to proper timing for the actual launching of the Fleet Test were lengthy and at times frustrating, but none the less were very successful. The following is a listing of the more important of these functions:

Questions of liability were discussed with and resolved by M.I.T. attorneys.

Negotiated lease of Field Test Station site with the Cambridge Redevelopment Authority (Fig. 4).

Negotiated tentative contracts with petroleum equipment companies for bids on equipping field site with appropriate tankage, piping, pumps and blending apparatus.

Investigated and resolved regulatory requirements with the Massachusetts Bureau of Standards and the City of Cambridge for licensing and permits.

Resolved Field Station status with the M.I.T. Office of Sponsored Programs where the site was accepted as being "on campus" for the purpose of having M.I.T. provide utilities, maintenance, insurance, custodial services, snow removal, etc.

Initiated and completed process for allocation of fuel stocks for the Program from the Federal Energy office in Boston and Washington.

Resolved MIT/OSHA safety regulations regarding storage and handling of automotive fuels on campus.

Worked on an informational program aimed at enlisting M.I.T. personnel to participate in the Program.

Established contact with Atlantic Richfield Co. through the M.I.T. Industrial Liaison Office for gratis supply of "Arconol" (tert-butanol, to stimulate methyl-fuel).

Contacted Consumer Union and paid a site visit to their Orange, Connecticut Test Station to observe some of the fuel economy runs.

Site visit to the Massachusetts Fuels Testing Station to determine first hand their methods for testing fuel volatilities.

Site visit to University of Nebraska to observe their fleet test ideas using "Gasahol" (ethanol/gasoline blends) in state-owned vehicles, test was not quite underway yet.

Negotiated tentatively the use of local race tracks for vehicle test runs in Revere, Norwood and Taunton, Mass.

Retained space at M.I.T. for instrumentation of initial test vehicles.

Materials and equipment were purchased to conduct preliminary economy test runs.

Mapped out certain portions of Route 2 in Belmont, Mass. for proposed highway test runs and made a number of trial test economy runs on different vehicles (Appendix B).

Designed and built instrumentation such as electronic accelerometer, 5th wheel, recording devices and precision buret economy test apparatus.

Set up a small test lab and acquired 22 different fuel samples to test separation of methanol/gasoline blends at low temperatures.

Attended conferences on the use of methanol as an alternative automotive fuel in Henniker, N.H. and Ann Arbor, Michigan.

Remained in contact with other methanol fleet research groups, U.C. Santa Clara, California (pure methanol fleet test) and the University of Nebraska "Gasahol" fleet test.

Current Status

Fleet test activities were terminated in February 1975 as a result of the decision by the M.I.T. Energy Laboratory to discontinue efforts to obtain external funding for the fleet test as an Energy Laboratory program. This decision followed a review of the prospects of obtaining suitable funding, of the value of the technical information which might come out of the program, and of the appropriateness of the M.I.T. resources and environment for this type of program.

References

1. Engineering Foundation Conference: "Methanol as an Alternative Fuel," New England College, Henniker, New Hampshire, 1974. Environmental Protection Agency Conference, "Methanol an Alternate Fuel," Ann Arbor, Michigan, October, 1974.
2. "Evaluation of Driveability Test Procedure, 1971 Yuma Program". Coordinating Research Council, Inc. CRC Report No. 455, June 1973. "Driveability Evaluation in Cool Weather," Coordinating Research Council Inc., CRC Report No. 439, December 1970. "CRC Revised Road Rating Techniques," Coordinating Research Council Inc. CRC Report No. 436, July 1970.
3. "Vapor-Liquid Ratio of Gasoline," ASTM:D2533-66T.
4. "Vapor Pressure of Petroleum Products" (Reid Methanol) ASTM:D323-58.

7. SUMMARY OF MAJOR FINDINGS

Methanol, alone or blended with gasoline, is a potential future automotive fuel. The most important questions to be answered relate to the impact its use would have on engine operation and emissions, and on fuel handling operations. Our studies have examined some of the fundamental aspects of spark-ignition engine operation with methanol alone, methanol-water mixtures and methanol-gasoline blends, and the phase stability characteristics of these blends.

The phase stability studies have quantified the tendency for traces of water to cause separation of blends into organic and aqueous phases at particular temperatures, and shown this to be a strong function of methanol content, water content, gasoline composition and added solubilizer for methanol/water. It was found possible to enhance the solvent power of gasoline with solubilizers such as benzyl alcohol. The quantity of solubilizer required is significant, however.

The engine results with methanol-gasoline blends show closely comparable emissions and efficiency to gasoline alone. There is a slight extension of the lean limit of operation. These results confirm that the major effect observed in vehicles with blends is the leaning out of the mixture which automatically occurs in a conventional carburetor due to the lower energy density of methanol, unless correcting adjustments are made.

Methanol alone significantly extends the lean limit of operation, and permits operation at much higher compression ratios with corresponding improvements in efficiency. The vaporization characteristics of methanol would require substantial changes to conventional carburetion technology to obtain acceptable engine start-up characteristics over all ambient conditions.

It is our assessment that additional basic research to characterize methanol as an automotive fuel is worthwhile. The primary question regarding its use remains its cost. But the quantification of its properties as an automotive fuel is incomplete and additional research will better define its potential and its problems.